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THE
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THE

PHYSICAL REVIEW

THE MAGNITUDE OF THE K-ABSORPTION DISCONTINUITY

By F. K. Richtmyer*

Abstract

Mass absorption coefficients for wave-lengths on both sides of the K limit. (1) *Experimental results for six metals.* Using a water cooled Mo tube, absorption measurements were made for a sufficient range of wave-lengths in each case to determine the constants in the equations for the mass absorption coefficients above and below the K absorption discontinuity. $\mu_K/\rho = K_K\lambda^3 + \sigma/\rho$; $\mu_L/\rho = K_K\lambda^3 + \sigma/\rho$, in which σ/ρ is the scattering coefficient, with a value of 1 or less. λ is in angstrom units. τ_a is the atomic absorption coefficient at the K limit, corrected for scattering.

	Mo(42)	Ag(47)	Sn(50)	W(74)	Au(79)	Pb(82)
$k_K =$	375	545	595	1870	2230	2570
$k_L =$	50	70	90	330	395	476
$k_K/k_L =$	7.5	7.8	6.6	5.65	5.65	5.40
$\tau_a(10^{-21}) =$	13.3	11.0	8.90	3.19	2.57	2.37

(2) *Comparison with theories.* $(k_K/k_L - 1)$ is the ratio of the number of photoelectrons originating in the K and L levels for x-rays just shorter than the K limit. It is shown that the theories of Thomson, of Compton, and of de Broglie lead to the same values of k_K/k_L, which increase with decreasing atomic number in agreement with experiment except that they are about twice too large. Kramers' formula gives a value which does not vary with N and which agrees well with the experimental values for Mo to Pb, but it applies only to a single electron around the nucleus. A formula modified by use of Bohr's theory of energy levels to remove this restriction gives values nearly three times too large. No present theory, then, is supported by these experimental results.

Introduction

SEVERAL attempts[1,2,3,4] have been made to obtain, on theoretical grounds, the equation

$$\tau_a = CN^4\lambda^3 \tag{1}$$

which has been found by experiment to represent the relation between the atomic fluorescent absorption coefficient τ_a for x-rays of wave-length λ absorbed by a substance of atomic number N. C is a constant for all

---

* This work has been made possible by a grant to the writer, from the Heckscher Research Council of Cornell University.

[1] J. J. Thomson, Conduction of Electricity through Gases, 2d. Ed., p. 321.

[2] L. de Broglie, Journ. de Phys. et Rad. **3**, 33 (1922).

[3] A. H. Compton, Nat. Res. Council, Bul. **20**, 37 (1922).

[4] H. A. Kramers, Phil. Mag. **46**, 836 (1923).

elements on the short wave-length side of the K absorption limit, and has a numerical value[5] of 22.4×10^{-27}, λ being expressed in angstrom units. At the K limit the value of C decreases abruptly. If we put

$$R_{\mathrm{L}}^{\mathrm{K}} = \frac{C_{\mathrm{K,L}\ldots}}{C_{\mathrm{L}\ldots\ldots}} \tag{2}$$

where $C_{\mathrm{K,L}\ldots}$ is the value of C on the short wave-length side of the K limit and $C_{\mathrm{L}\ldots}$ that on the long wave-length side, then the ratio $R_{\mathrm{L}}^{\mathrm{K}}$ of the two values of C depends on the atomic number of the absorber, being less for elements of higher atomic number. For example, for elements in the neighborhood of Ag $R_{\mathrm{L}}^{\mathrm{K}}$ is about 8. For elements in the neighborhood of Pt it is about 5.5.

The several theoretical formulas above referred to, although obtained on the basis of widely different considerations, agree with experiments in assigning 4 and 3 as the exponents of N and λ respectively in Eq. (1). There is a disagreement, however, with experiment, in respect to not only the magnitude of $R_{\mathrm{L}}^{\mathrm{K}}$ but also its variation with atomic number. The extent to which any theoretical formula agrees with experiment in predicting the correct value of $R_{\mathrm{L}}^{\mathrm{K}}$ is therefore a more discriminating test of the correctness of the formula than are the coefficient of N and λ.

A knowledge of the precise value of $R_{\mathrm{L}}^{\mathrm{K}}$ is of prime importance in connection with further extensions of our present very incomplete "picture" of the interaction between radiation and matter. So far as it goes this picture is quite precise with regard to the sequence of the main events in the (fluorescent) absorption of x-rays. Thus, if a monochromatic x-ray beam of frequency ν and of quantum energy $h\nu$ strikes an absorber the frequency of whose K absorption limit ν_{K} is less than ν, the first process is the photo-electric expulsion of electrons from the several electron levels[6] in the atom according to the well known equation

$$h\nu = W + h\nu_{\mathrm{K,L,M}\ldots} \tag{3}$$

where $h\nu_{\mathrm{K,L,M}\ldots}$ represents in turn the work necessary to remove electrons from the K, L, M . . . levels respectively and W is the residual kinetic energy of the photo-electron originating in the K, L, M. . . level. The vacant place in the atom is then filled by an electron from an outside level, or from infinity, and the K, L, M. . . fluorescent radiation results. It is to be remembered, however, that, irrespective either of what ultimately becomes of the energy given to the electron or whether a K, L or M electron is expelled, *each photo-electron removes from the incident beam* an amount of energy $h\nu$. By dividing by $h\nu$ the total amount of energy removed by the absorber in this fluorescent process, the total *number* of photo-electrons produced under given conditions, may be obtained. We have at present no way of measuring with acceptable precision the actual magnitude of this absorbed energy, but by comparing the fluorescent absorption coefficient on the short wave-length side of the K absorption limit with that on the long wave-length side, it is possible to get the ratio of the total number of (K+L+M . . .) photo-electrons to the total number of (L+M. . .) photo-electrons. Thus

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[5] F. K. Richtmyer and F. W. Warburton, Phys. Rev. **22,** 539 (1923).

[6] See, for example, the beautiful experiments of Robinson, Proc. Roy. Soc. **104,** 455 (Nov. 1923).

$$R_{\mathrm{L}}^{\mathrm{K}}=\frac{\text{total number of K+L+M+ . . . photo-electrons}}{\text{total number of L+M+. . . photo-electrons}} \tag{4}$$

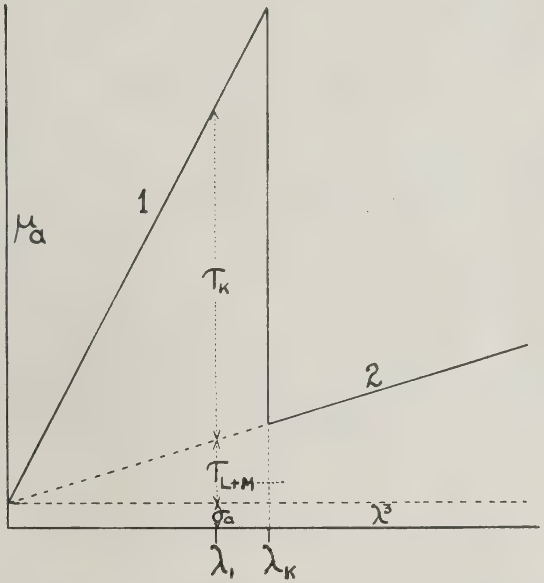

Fig. 1. Variation of the atomic absorption coefficient with the cube of the wave-length.

This relation is shown graphically in Fig. 1, which represents diagrammatically,[7] to approximate scale, the linear relation between the atomic absorption coefficient μ_a and the cube of the wave-length on both sides of the absorption limit. Thus, if radiation of wave-length $\lambda_1<\lambda_{\mathrm{K}}$ falls on the absorber, we may regard the atomic absorption coefficient at that wave-length as being made up of several parts: (1) a part τ_{K} due to the energy removed from the beam by the expulsion of K photo-electrons; (2) a part $\tau_{\mathrm{L+M+\ldots}}$ due to the expulsion of L+M+. . . photo-electrons; and (3) a part σ_a due to the energy removed by scattering. Although σ_a and its variation with wave-length are of very great theoretical significance, it is responsible for only a small proportion of the energy removed from the incident beam, especially in those elements and for those wavelengths for which $R_{\mathrm{L}}^{\mathrm{K}}$ is known. Hence to a first approximation σ_a may be considered as constant and equal to the intercept on the μ_a axis, of the absorption curves on both sides of the K limit. Accordingly it is obvious that the ratio

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[7] F. K. Richtmyer, loc. cit. 10, p. 27.

$$(\tau_{\mathrm{K}}+\tau_{\mathrm{L+M+}}\ldots)/(\tau_{\mathrm{L+M+}}\ldots) = R_{\mathrm{K}}^{\mathrm{L}} \tag{5}$$

gives the relative number of the several "kinds" of photo-electrons, and hence the relative probabilities of the expulsion of electrons from the several energy levels within the atom. It is this probability which has been computed by the several writers[1,2,3,4] and which it is desired to compare with experiment.

DATA ON THE K DISCONTINUITY

The experimental data on the magnitude of the K absorption discontinuity are very meager. Discarding, as of comparatively little value, the measurements with heterogeneous radiation, there are collected in columns 3, 4, and 5 of Table I data obtained by use of monochromatic radiation by Wingardh,[8] Allen,[9] and the writer.[10] At the December 1923 meeting of the American Physical Society, Mr. F. W. Warburton[11] in collaboration with the writer presented, in brief form, some data on the K discontinuities for several elements. The data were not regarded as very satisfactory, and publication of the results in full was delayed until further measurements could be made. Other investigations have pre-

TABLE I

Element	Atomic Number	Values of $R_{\mathrm{L}}^{\mathrm{K}}$			
		Wingardh[8]	Allen[9]	Richtmyer[10]	Richtmyer and Warburton[11]
Mo	42			8.7	7.5
Ag	47	8.0*	7.1*	7.3	7.8
Sn	50		8.9†		6.6
W	74		6.0		5.65
Pt	78		5.3		
Au	79		5.0		5.65
Pb	82		4.5		5.40
Bi	83		4.1		

* Computed from data given in reference.

† Computed by combining data given by Allen (loc. cit.[9]), with data given by Bragg and Pierce (Phil. Mag. **28**, 626, 1914).

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[8] K. A. Wingardh, Dissertation, Lund (1923).

[9] S. J. M. Allen, Phys. Rev. **24,** 1 (July 1924).

[10] F. K. Richtmyer, Phys. Rev. **18,** 13 (July 1921).

[11] F. W. Warburton and F. K. Richtmyer, Phys. Rev. **23,** 291 (Feb. 1924).

vented further progress on the work; so in this paper are presented the data of Warburton and Richtmyer, with some minor corrections.

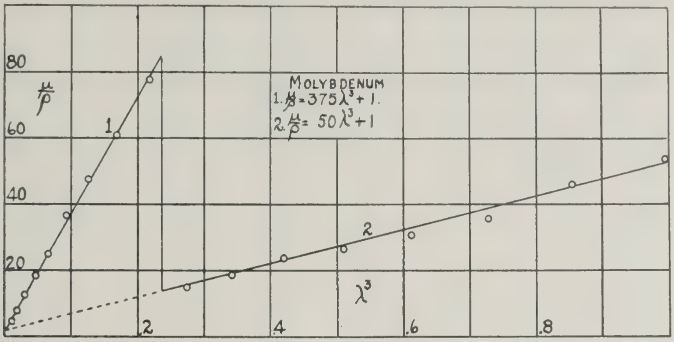

Fig. 2. Variation of the mass absorption coefficient of molybdenum with the cube of the wave-length.

The method of measuring coefficients of absorption of x-rays is too well known to require comment. The apparatus used for the present investigation has been previously described.[12] For obtaining sufficient energy at

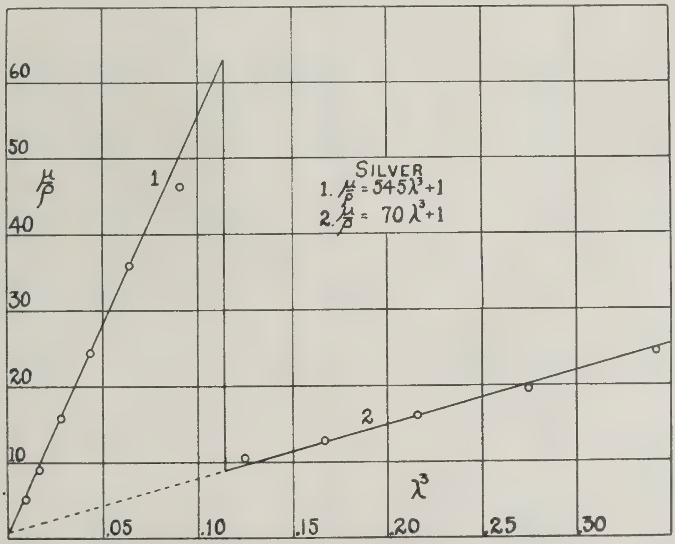

Fig. 3. Variation of the mass absorption coefficient of silver with the cube of the wave-length.

the longer wave-lengths herein reported, a water-cooled molybdenum tube was used. The writer is indebted to Dr. W. D. Collidge of the General Electric Company, for the use of this tube.

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[12] F. K. Richtmyer and F. W. Warburton, Phys. Rev. **22,** 539 (1923).

Observations were made through the K absorption limits of Mo, Ag, Sn, W, Au, and Pb. The data are shown in graphical form in Figs. 2-7, in which the mass absorption coefficients for the several elements are plotted as functions of the cube of the wave-length. In these graphs the K absorption discontinuity is represented by a vertical line, since, as has been recently shown by the writer,[13] the K discontinuity for silver shows no measurable structure and is sharp to at least .0001A. Since, to a very

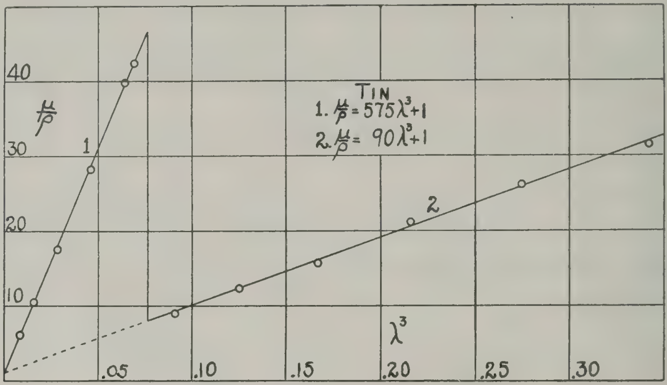

Fig. 4. Variation of the mass absorption coefficient of tin with the cube of the wave-length.

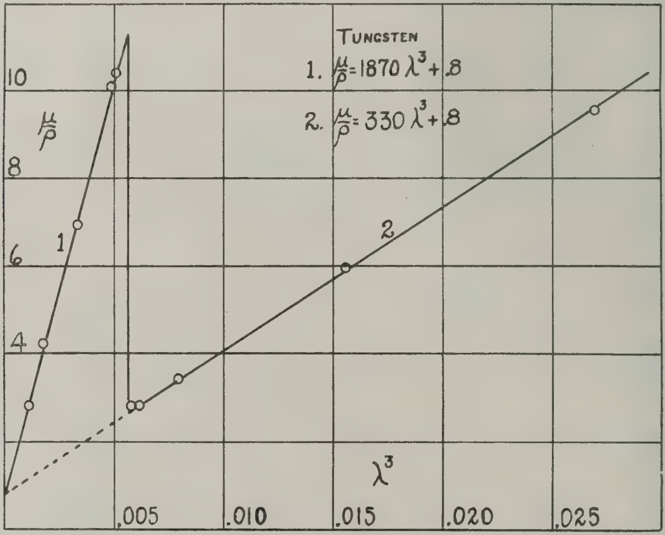

Fig. 5. Variation of the mass absorption coefficient of tungsten with the cube of the wave-length.

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[13] F. K. Richtmyer, Phys. Rev. **26**, 724 (Dec. 1925).

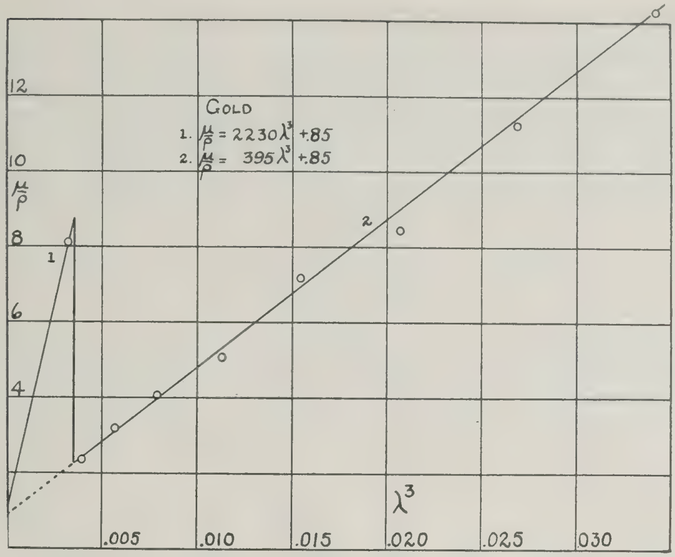

Fig. 6. Variation of the mass absorption coefficient of gold with the cube of the wave-length.

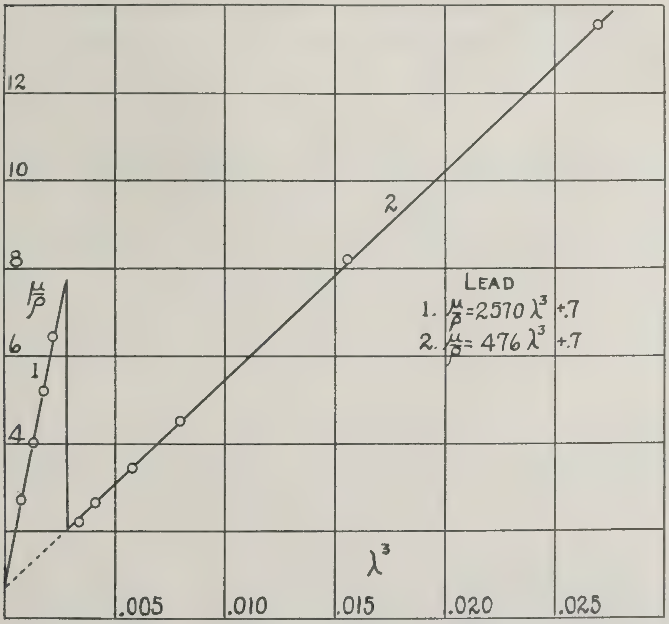

Fig. 7. Variation of the mass absorption coefficient of lead with the cube of the wave-length.

close approximation at least, the graphs, both above and below the K limit are straight lines, and have nearly, if not quite, identical intercepts on the μ/ρ axis, it is obvious that the values of R_L^K are given by the ratios of the slope of the graph on the short wave-length side of the limit to that on the long wave-length side. These slopes are collected in columns 2 and 3 of Table II, the values k_K and k_L being the values in the equations

$$\mu_K/\rho = k_K\lambda^3 + \sigma/\rho \tag{6}$$

$$\mu_L/\rho = k_L\lambda^3 + \sigma/\rho \tag{7}$$

TABLE II

The values of k_K and k_L are the slopes of the curves in figs. 2-7; $(\mu/\rho)_{max}$ is the maximum value reached by μ/ρ just at the short wave-length side of the K limit; $(\tau/\rho)_{max}$ is obtained by subtracting from $(\mu/\rho)_{max}$ the intercept on the μ/ρ axis; n gives the number of atoms per gram; $(\tau a)_{max}$ is obtained by dividing $(\tau/\rho)_{max}$ by n; R_L^K is the ratio k_K/k_L.

Element	k_K	k_L	$(\mu/\rho)_{max}$	$(\tau/\rho)_{max}$	n	$(\tau a)_{max}$	R_L^K
Mo 42	375	50	85.0	84.0	6.31×10^{21}	13.3×10^{-21}	7.5
Ag 47	545	70	63.0	62.0	5.61	11.0	7.8
Sn 50	595	90	46.5	45.5	5.11	8.90	6.6
W 74	1870	330	11.3	10.5	3.29	3.19	5.55
Aw 79	2230	395	8.8	7.9	3.07	2.57	5.65
Pb 82	2570	476	7.8	6.9	2.91	2.37	5.4

μ_K and k_K refer to the short wave-length side of the limit; μ_L and k_L to the long wave-length side. From what has been said before it is evident that the ratio R_L^K is given by

$$R_L^K = k_K/k_L$$

These ratios are tabulated in column 8 of Table II and also for comparison with results of others, in column 6 of Table I.

A glance at Table I makes it obvious that the data warrant only the general conclusions that there is agreement on the order of magnitude of the discontinuity and that the values of R_L^K range from around 5.5* for the heavier elements to 7.5 or 8 for elements in the neighborhood of silver.

---

* A careful examination of Allen's data makes it seem probable that the values given by him for the heavier elements are too low. This statement is based on the circumstance that, beginning with tungsten, Allen's values of μ/ρ on the short wave-length side of the K limit *decrease*, at any given wave-length, with *increasing* atomic number, a result quite in opposition to data obtained by other investigators. Allen's curves reveal the fact that the *apparent* width of his K discontinuities from *silver* to lead, is the *same* for each element and is equal to approximately .02A. This defines his slit width, since the writer has shown[12] that for the K limit of the heavier elements, the apparent width of the discontinuity is due entirely to the finite width of slits. One suspects, therefore, that with a rather wide slit, when working near the absorption limit, there may have been a sufficient admixture of scattered radiation from the long wave-length side of the limit to reduce appreciably the observed mass absorption coefficient.

DISCUSSION OF RESULTS

There are several points of passing interest, in connection with these results, which it may be not inappropriate to mention in order to call attention to the relative magnitude of the several discontinuities.

Fig. 8 shows to scale, each at the wave-length of its K absorption limit, the relative magnitudes of the K discontinuities for each of the six elements investigated. Here τ_a is the fluorescent atomic absorption coefficient* after making the rather unsatisfactory correction for scattering. It is to be noted that the *absolute* magnitude of the discontinuity increases rapidly with decreasing atomic number. That is, molybdenum, just at the short wave-length side of its absorption limit is a much better absorber than is lead at the short wave-length side of its limit.

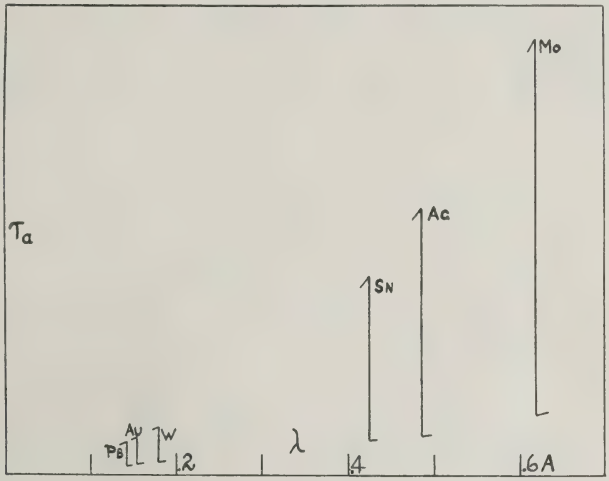

Fig. 8. Showing to scale the relative magnitudes of the K absorption discontinuities for the six elements investigated.

This result is of course to be anticipated from the well known laws of absorption, combined with Moseley's law, which, for the K absorption limit may be written in the form

$$\lambda_K = c'/(N-b)^2$$

where N is the atomic number, and b and c' are constants. If this value of λ_K be introduced into Eq. (1) there results

$$\tau_{\max} = c''\, N^4/(N-b)^6 \tag{8}$$

---

* If the observed values of the mass absorption coefficient μ/ρ be corrected by subtracting the value of the mass scattering coefficient σ/ρ, as determined by the intercept on the μ/ρ axis in Figs. 2-7, one obtains τ/ρ the *fluorescent* mass absorption coefficient. Thus $\mu/\rho = \tau/\rho + \sigma/\rho$. If the values of τ/ρ be divided by the number of atoms per gram in each case, one obtains τ_a, the atomic fluorescent absorption coefficient. And as explained above $\tau_a = \tau_K + \tau_L + \tau_M +, \ldots$

where $\tau_{\max}$ is the *maximum* value of the atomic absorption coefficient just at the short wave-length side of the K limit, and c'' is another constant, the assumption being made, of course, that Eq. (1) holds rigorously up to the K limit. If b be neglected in comparison with N, it follows that the maximum value of the atomic fluorescent absorption coefficient just at the short wave-length side of the K limit should be proportional to N^{-2}. A convenient check on Eq. (8) is the determination of b. This can be readily done by putting the equation in the form

$$(c''N^4/\tau_{\max})^{1/6}=N-b \qquad (9)$$

and plotting a graph between $(N^4/\tau_{\max})^{1/6}$ and N.* This graph is shown in Fig. 9, from which it is seen that the value of b which best agrees with these data is about 7.5, much larger than the accepted value of b in Moseley's equation. The data are not sufficiently precise to determine whether this large value of b is due to experimental error, or whether it is due to the fact that Eq. (1), as is well known, is only a close approximation to the true formula.

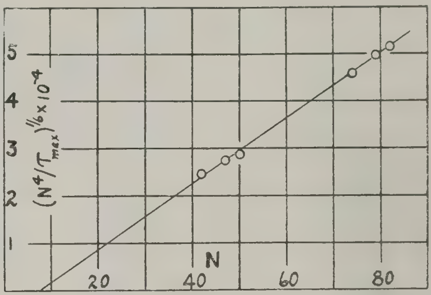

Fig. 9. Graphical determination of b in the term $(N-b)$ of Eq. (8).

COMPARISON WITH THEORY

The experimental values of R_L^K as a function of N are shown by the circles in Fig. 10. The points plotted for molybdenum and silver are the average of those given in Table I. The remaining points are those given in the last column of Table I. While it is obvious that the data do not warrant an attempt to ascertain an empirical relation between R_L^K and N, nevertheless they are sufficient to serve as a check, even though a rough one, on the several theories proposed.

Thomson's theory.[1] This well known theory was proposed by Thomson at least as early as 1903. It is based on the assumption that the electron

* Values of $(N^4/\tau_{\max})^{1/6}$ were computed from the data given in columns 1, 4, 5, 6 and 7 of Table II, λ being expressed in angstroms.

is bound to a fixed position in the atom by simple harmonic forces. The displacement of the electron from this equilibrium position is then computed when a pair of rectangular but oppositely directed pulses, each of thickness *d*, passes over the electron. The potential energy stored up in this displacement is extracted from the pair of pulses and is emitted as fluorescent energy of wave-length λ_0 after the pulse has passed. This leads to the following absorption coefficient per electron, τ_e, *for a single pair of pulses*

$$\tau_e = 4\pi^3 \frac{e^2}{mc^2} \frac{1}{\lambda_0^2} d^3 , \tag{10}$$

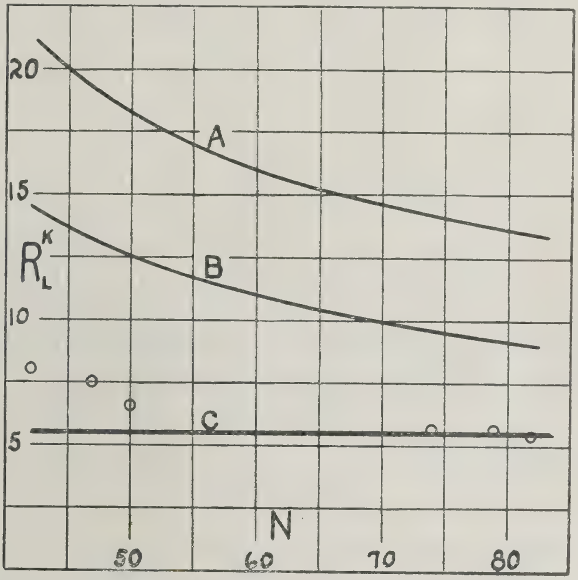

Fig. 10. Variation of the absorption discontinuity with atomic number. Curve A: Kramers' theory as modified by Eq. (26). Curve B: Theories of Thomson (Eq. (13)), of Compton (Eq. (15)), and of de Broglie (Eq. (21)). Curve C: Kramers' original theory (Eq. (24)). The circles represent actual observations.

or if we identify *d* with $\lambda/2$, where λ is the wave-length of the incident x-rays, we have

$$\tau_e = \frac{\pi^3}{2} \frac{e^2}{mc^2} \frac{1}{\lambda_0^2} \lambda^3 . \tag{11}$$

It is interesting to point out that on Thomson's theory the term d^3, or in more modern terms λ^3, is obtained by the following steps. (1) The electron experiences a uniform acceleration for a time which is proportional to *d* and is therefore displaced through a distance proportional to d^2. (2) The potential energy stored up against return forces is proportional to d^4; but the incident energy must be proportional to d. (3) The absorption coefficient, which is the ratio of absorbed to incident energy, is therefore proportional to d^3. The atomic absorption coefficient τ_a is obtained by summing up the term $1/\lambda_0^2$ for each electron in the atom, hence

$$\tau_a = \frac{\pi^3}{2} \frac{e^2}{mc^2} \sum \frac{n_0}{\lambda_0^2} \lambda^3 \tag{12}$$

where for the atom under consideration n_0 represents the number of electrons emitting characteristic radiation of wave-length λ_0. Eq. (12) can be put into a form to be compared with more recent formulas by using the relation

$$\frac{1}{\lambda_0^2} = \frac{h^2 \nu_0^2}{h^2\, c^2} = \frac{E_0^2}{h^2\, c^2}$$

which gives

$$\tau_a = \frac{\pi^3}{2} \frac{e^2}{mh^2c^4} (n_K E_K^2 + n_L E_L^2 + \cdot \cdot \cdot) \lambda^3 \tag{13}$$

where, in modern notation, n_K, n_L . . . stand for the number of electrons in the K, L . . . levels respectively and E_K, E_L . . . are the corresponding binding energies. To check this with experiment, (13) gives for Bi in the K region, assuming $n_K = 2$, $n_L = 8$, $n_M = 18$ and averaging the multiple values of E_L and E_M usually found in tables,

$$\tau_a = 5.20 \times 10^6\ \lambda^3$$

whereas (1) gives for B_i

$$\tau_a = 1.06 \times 10^6\ \lambda^3$$

It appears therefore that Thomson's formula gives a value of τ_a about five times too large.

There are reasons why we might expect (13) to give too large values. The discussion is based on the passage of a *single* pair of pulses over the electron. If a *train* of pulses is considered, each succeeding pulse produces an additional displacement and an increased restoring force. The result is that less energy is removed per pulse the greater the displacement. For a large number of pulses it is obvious that the average energy removed per pulse would be less than for the first pulse; i.e. the absorption coefficient for a wave train should be less than for a single pulse.

It is observed* that the introduction into (13) of Moseley's approximate law $\nu \propto N^2$ for the relation between an absorption limit and atomic number leads directly to an equation of the form of (1).

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* See also A. H. Compton, Phys. Rev. **14**, 249 (1919).

Compton's theory. This is somewhat similar to Thomson's theory in that it applies the fundamental laws of dynamics to "electrically charged particles capable of executing damped harmonic oscillations." An equation for the absorption coefficient per electron is then derived which involves the damping coefficients of the forced and of the free vibrations and the corresponding frequencies. This equation is simplified by approximation, and the exponent of λ is determined by an empirical evaluation, the resulting expression for the *atomic* absorption coefficient being given by

$$\tau_a = 2\pi \frac{e^2}{mc^4}\left(n_{\mathrm{K}} \frac{1}{\lambda_{\mathrm{K}}{}^2} + n_{\mathrm{L}} \frac{1}{\lambda_{\mathrm{L}}{}^2} + \cdot\ \cdot\ \cdot\ \cdot \right)\lambda^3 \tag{14}$$

which, when put in the form

$$\tau_a = 2\pi \frac{e^2}{mh^2c^4}(n_{\mathrm{K}}E_{\mathrm{K}}{}^2 + n_{\mathrm{L}}E_{\mathrm{L}}{}^2 + \cdot\ \cdot\ \cdot)\lambda^3 \tag{15}$$

is identical with (13) except for the factor involving π.

For bismuth, this gives

$$\tau_a = 2.10 \times 10^6\ \lambda^3$$

a result approximately twice the experimental value. Compton's formula does not give an independent theoretical justification for the λ^3 term.

de Broglie's theory.[2] This theory is based on the assumption that it is possible to set up conditions of equilibrium between atoms and a radiation field such that the rate of absorption of energy by the atoms in the process of the *photo-electric emission of electrons* is just equal to the rate of emission of energy as a result of the converse process, namely the "de-ionizing" of atoms by the free electrons. The equation to express this fact assumes the following form

$$N_{i_p} A_{i_p}^{n} E_p dt = \frac{1}{\eta_p} N_n \int_{\nu_p}^{\infty} h\nu F(\nu)\ \rho(\nu\ ,\ T) d\nu\ dt \tag{16}$$

where $A_{i_p}^{n}\ dt$ represents the fraction of ionized atoms, N_{i_p} per cc which take up free electrons in time dt and return to the normal state n, from the ionized state i_p, giving out energy E_p per atom; N_n is the number of normal atoms per cc taking part in the equilibrium process; $F(\nu)$ is a function of the frequency which states the fraction of normal atoms which become ionized in unit time, for unit density of the radiation of frequency ν, the energy density being given by Wien's equation

$$\rho(\nu,\ T)d\nu = (8\pi h/c^3)\nu^3 e^{-h\nu/kT} d\nu. \tag{17}$$

$1/\eta_p$ represents the fractional part of the absorbed energy which is returned in the corresponding fluorescent radiation. If $F(\nu)$ be evaluated and multiplied successively by (1) the number of atoms $N\,dx$ per square centimeter of an absorbing material of thickness dx, (2) the energy *density* of the incident radiation of frequency ν, and (3) the energy $h\nu$ absorbed by each atom in the process of ionization, the result is the rate of absorption of energy. If this result be divided by the rate at which energy is incident on the square centimeter we have the absorption coefficient which is found to be

$$\tau_a = (1/8\pi ckT)\lambda^3 \sum A_{i_p}^{n} E_p \eta_p \,. \tag{18}$$

The summation is to be extended to all the electrons of the atom. It is assumed that

$$\eta_p A_{i_p}^{n} = KE_pT \tag{19}$$

K is evaluated and found to be

$$K = \frac{8\pi^2}{c^3}\,\frac{k}{h^2}\,\frac{e^2}{m} \tag{20}$$

If (19) and (20) be put in (16) and the result extended to all the electrons of the atom we have

$$\tau_a = \pi(e^2/mh^2c^4)(n_K E_K{}^2 + n_L E_L{}^2 \cdot \cdot \cdot \cdot)\,\lambda^3 \tag{21}$$

a result identical with Thomson's value, Eq. (13), except for the factor involving π. For bismuth Eq. (21) gives, for $\lambda < \lambda_K$,

$$\tau_a = 1.14 \times 10^6 \lambda^3$$

in excellent agreement with experiment. It is to be observed that the λ^3 term appears in (18) because of the introduction of Wien's Eq. (17) in which appears the term ν^3.

Kramers' Theory. This has several points in common with deBroglie's theory. Both assume Wien's law of energy distribution and the possibility of thermodynamic equilibrium. Kramers then starts with the assumption that

$$NP_nQ_{n\to i} = NP_iQ_{i\to n} \tag{22}$$

where P_n represents the fraction of a total number N of atoms which are in an n or normal state and $Q_{n\to i}$ represents the fraction of these per second which pass from the normal to the ionized state i. Similarly P_i represents the fraction of N atoms which are in the ionized state, a fraction $Q_{i\to n}$ of which return per second to the n state. P_n and P_i are connected by Boltzman's probability principle. $Q_{n\rightarrow i}$ involves the spectral energy density of the exciting radiation (given by Wien's law) and the atomic absorption coefficient, τ_a' which, since τ_a' has the dimensions of an area, may be regarded as "the effective cross-section" of an atom for intercepting radiation. $Q_{i\rightarrow n}$ on the contrary involves the inverse process, namely the effective cross section τ_β of an ionized atom for intercepting electrons. A simple relation is thus established between τ_a' and τ_β. By aid of the correspondence principle and the classical laws of radiation of an electron describing an orbit *past a positively charged nucleus Ne*, the value of τ_β is determined. The final value of τ_a' may be put in the form

$$\tau_a' = \frac{64\pi^4}{3\sqrt{3}} \frac{e^{10}m}{c^4\ h^6} g' \frac{1}{k^4(k+1)} N^4\lambda^3 \tag{23}$$

where τ_a' refers to the absorption coefficient of a nucleus Ne, with a *single* electron in the k quantum orbit, and g' is a constant "which does not differ much from unity." If it be assumed that we can compute the *atomic* absorption coefficient τ_a by summing up (23) for all the electrons of a neutral atom of atomic number N we have

$$\tau_a = \frac{64\pi^4}{3\sqrt{3}} \frac{e^{10}m}{c^4\ h^6} g' \left(\frac{2}{1.2} + \frac{8}{2^4\ 3} + \frac{18}{3^4\ 4}\right) N^4\lambda^3 \tag{24}$$

where 2, 8, 18 . . . . represent the respective number of electrons in quantum rings 1, 2, 3. . . . .

Computing, as before, the absorption coefficient for bismuth we have (assuming $g'=1$),

$$\tau_a = 60\times 10^4\lambda^3\ ,$$

a value which is about half the experimental value.

Although difficult to trace, it appears that the term λ^3 appears in Kramers' formula on account of the introduction of Wien's law, and the term N^4 apparently comes from the application of classical electrodynamics to the radiation of an electron as it passes a nucleus of charge Ne.

As Kramers points out, Eq. (23) is derived for the case of a nucleus of charge Ne and a single electron. It can therefore be expected to be only an approximation when applied to all the electrons of an atom. The approximation may be expected to be of the same order as is found in the case of Bohr's theory of the hydrogen spectrum when applied to elements of higher atomic number. Indeed, by use of Bohr's equation for the energy of a given quantum orbit k, namely

$$E_k = h\nu_k = (2\pi^2 mN^2e^4/h^2)\ (1/k^2)$$

we can re-write (23) as follows

$$\tau_a' = \frac{16}{3\sqrt{3}} g' \frac{e^4}{mh^2c^4} \frac{E_k{}^2}{k+1} \lambda^3 \tag{25}$$

It seems reasonable to extend Eq. (24) so as to include all the electrons of a neutral atom by writing

$$\tau_a = \frac{16}{3\sqrt{3}} g' \frac{e^4}{mh^2c^4} \left(\frac{n_{\mathrm{K}} E_{\mathrm{K}}{}^2}{1+1} + \frac{n_{\mathrm{L}} E_{\mathrm{L}}{}^2}{2+1} \cdot \cdot \cdot \right) \lambda^3 \tag{26}$$

If now, in using (26) we put in the *experimental* values of E_{K}, E_{L} . . . the formula should be freed of the limitation of a *single* electron around a nucleus Ne and should apply generally. Computing τ_a for bismuth in this way gives

$$\tau_a = 50 \times 10^4 \lambda^3 .$$

It is to be observed that (13), (15) and (21) are identical, except for the value of the factor involving π. However (26) differs from these three not only in the corresponding numerical factor, but in dividing each of the terms E^2 in the bracket by $(k+1)$. *It is in reality this factor $(k+1)$ which reduces the value of τ_a computed from (26) to about half the correct value.* If this factor be omitted the value of τ_a given by (22) is *correct within experimental error for $\lambda < \lambda_{\mathrm{K}}$.*

We are now in position to compare these several theories as regards their prediction of the magnitude of the K absorption discontinuity as expressed by the value of $R^{\mathrm{K}}_{\mathrm{L}}$. It is evident that Eqs. (13), (15), and (21) give identical values of $R^{\mathrm{K}}_{\mathrm{L}}$ namely:

$$R^{\mathrm{K}}_{\mathrm{L}} = \frac{n_{\mathrm{K}} E_{\mathrm{K}}{}^2 + n_{\mathrm{L}} E_{\mathrm{L}}{}^2 + n_{\mathrm{M}} E_{\mathrm{M}}{}^2 + \cdot \cdot \cdot}{n_{\mathrm{L}} E_{\mathrm{L}}{}^2 + n_{\mathrm{M}} E_{\mathrm{M}}{}^2 + \cdot \cdot \cdot} \tag{27}$$

while for (24) $R^{\mathrm{K}}_{\mathrm{L}}$ is independent of N and is given by

$$R^{\mathrm{K}}_{\mathrm{L}} = \frac{1 + 1/6 + 1/18 + \cdot \cdot \cdot}{1/6 + 1/18 + \cdot \cdot \cdot} = 5.5 \tag{28}$$

For (26) we have, on the contrary,

$$R^{\mathrm{L}}_{\mathrm{K}} = \frac{\frac{n_{\mathrm{K}}}{2} E_{\mathrm{K}}{}^2 + \frac{n_{\mathrm{L}}}{3} E_{\mathrm{L}}{}^2 + \frac{n_{\mathrm{M}}}{4} E_{\mathrm{M}}{}^2 \cdot \cdot \cdot}{\frac{n_{\mathrm{L}}}{3} E_{\mathrm{L}}{}^2 + \frac{n_{\mathrm{M}}}{4} E_{\mathrm{M}}{}^2 \cdot \cdot \cdot} \tag{29}$$

In evaluating (27), (28) and (29) it is assumed that it is unnecessary to include limits beyond the M limits, and that the values of n_{K}, n_{L} and n_{M}

are respectively 2, 8 and 18. The values of E_K, E_L and E_M used are those obtained partly from Sommerfield's "Atomic Structure and Spectral Lines," and partly from Robinson (Proc. Roy. Soc. **104,** 455 (Nov. 1923). There has been no attempt to weight the multiple values of E_L and E_M; the average values of E_L^2 and E_M^2 have been used. The data are shown in Table III. The values of R_L^K given by the two equations are shown graphically in Fig. 10, curve A corresponding to Eq. (29) (Kramers' theory as modified in Eq. (26)), and curve B to Eq. (27). The line C in Fig. 10 gives the ratio predicted by Kramers' original Eq. (24). It is seen that the observed values correspond most closely to Kramers' Eq. (24), but this agreement must be regarded as fortuitous, since there can be no doubt that a multiple charged nucleus with a *single* electron behaves quite unlike such a nucleus with its normal quota of electrons. The step from Eq. (23) to (24) cannot therefore be made without some modification. The suggested modification (26) however, gives values of R_L^K (curve A) entirely too large.

TABLE III

Element		E_K	E_L*	E_M*	R_L^K Eq. (27)	R_L^K Eq. (29)
Pb	82	6463	1080	233	9.1	13.4
Au	79	5940	985	207	9.2	13.5
W	74	5114	833	170	9.6	14.2
Sn	50	2148	311	50	12.4	18.2
Ag	47	1879	263	36	13.3	19.7
Mo	42	1473	197	27	14.4	21.3

* "Root-mean-square" values.

Values of E are given in terms of ν/R, where ν is wave-number and R is the Rydberg constant.

While these equations, therefore, do not give values of R_L^K which check closely with experiment, it is very significant that they predict in a qualitative way the variation of R_L^K with N. The experimental data themselves are by no means satisfactory, although probably correct to ten or twenty percent.

It is hoped to improve the precision with which these measurements can be made, and to obtain values of R_L^K for a larger number of elements.

CORNELL UNIVERSITY,
September 11, 1925.

PHYSICAL REVIEW JANUARY, 1926 VOL. 27

MEASUREMENT OF THE REFRACTION OF X-RAYS IN A PRISM BY MEANS OF THE DOUBLE X-RAY SPECTROMETER

By Bergen Davis and C. M. Slack

Abstract

In the double spectrometer used, x-radiation was reflected from a crystal surface A through a slit S on to a second crystal surface B, and thence to the ionization chamber. Surfaces A and B were obtained by splitting a single crystal of calcite. The curve obtained for Mo Kα by rocking B is a triangle with base about 8 seconds wide. The effect of interposing a *prism of aluminum* (angle 166°) between S and B was to shift the curve 5.62″ on the average, giving $1-\mu=1.68\times10^{-6}$. The value calculated from the Lorentz dispersion formula is 1.77×10^{-6}. For Cu Kα the shift was 5.53″ for a 116° prism, giving $1-\mu=8.4\times10^{-6}$ as compared with the calculated value 8.36×10^{-6}. The accuracy of this method is thus within 5 percent.

EVIDENCE of the direct refraction of x-rays on passing through a prism was long sought for without success. The effect is so minute that its direct detection is difficult.

Recently, however, the direct bending in a prism has been measured by the photographic spectrometer method in the laboratory of Professor Siegbahn.[1] Shortly afterward the direct refraction in a prism was measured by the authors,[2] using the single ionization spectrometer. A serious defect of the single ionization spectrometer for this purpose arises from the fact that the maxima of the energy curves are shifted not only by refraction but by the unsymmetrical absorption of the beam in the prism.

Refraction at the surface of a crystal in the case of crystal reflection had already been quite accurately measured by Bergen Davis and R. von Nardroff[3] and by C. C. Hatley,[4] using the ionization spectrometer.

The present paper describes the application of the *double x-ray spectrometer* to the measurement of refraction in a prism. This method is capable of considerable accuracy. A bending of the beam of x-rays as small as one-tenth second of arc can be observed when conditions are favorable.

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[1] Larsen, Siegbahn and Waller, Proc. Am. Phys. Soc., Phys. Rev. **25,** 235 (Feb. 1925)

[2] Bergen Davis and C. M. Slack, Proc. Am. Phys. Soc., Phys. Rev. **25,** 881 (June 1925).

[3] Bergen Davis and R. von Nardroff, Proc. Nat. Acad. Sc., **10,** (Feb. 1924) also (Sept. 1924).

[4] C. C. Hatley, Phys. Rev. **24,** 486 (Nov. 1924).

The method will be at once clear by reference to Fig. 1. *A* and *B* are two crystals of split Iceland-spar (calcite). The two reflecting surfaces are the divided halves of the same crystal. The surface of *B* on which the rays fall is the surface that coincided with the reflecting surface of *A* before cleavage. Care was taken to mount the crystals without abrading the reflecting surfaces in any way. The percent reflection and still more important, the narrowness of the "rocking" curves, depends on the virgin condition of these surfaces.[5]

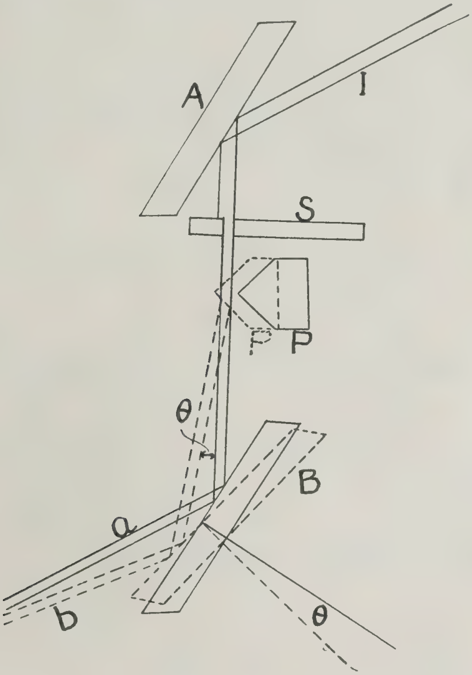

Fig. 1. The double x-ray spectrometer.

The narrow beam *I* of incident x-rays is reflected from crystal *A* through a limiting slit *S* to crystal *B*, and from *B* to the ionization chamber. Crystal *B* is mounted in such a way that it can be turned through a small measured angle as desired. This is accomplished by means of a long arm attached to the crystal table which is operated by a tangent screw. The hand wheel that turns the tangent screw is so divided that one scale division on the edge of wheel represents one-half second of arc of rotation of crystal. The details of this arrangement have been previously described (see Fig. 2 of Davis and Stempel[5]).

[5] Davis and Stempel, Phys. Rev. **17,** 608 (May 1921).

The beam of homogeneous x-rays after passing through slit *S* falls on crystal *B* and is reflected into the ionization chamber. This beam is marked *a* in Fig. 1. Maximum reflection is obtained when the reflecting planes of *B* are parallel to those of *A*. If now crystal *B* be turned (rocked) a small measured angle each side of this maximum position, energy distribution curves are obtained (curve *a*, Fig. 2). By careful adjustment of the crystals these rocking curves could be made quite narrow. The width at half-maximum was less than 6″ of arc in the case of Mo Kα radiation. The position of the maximum of the curves could be determined to about one-tenth second of arc.

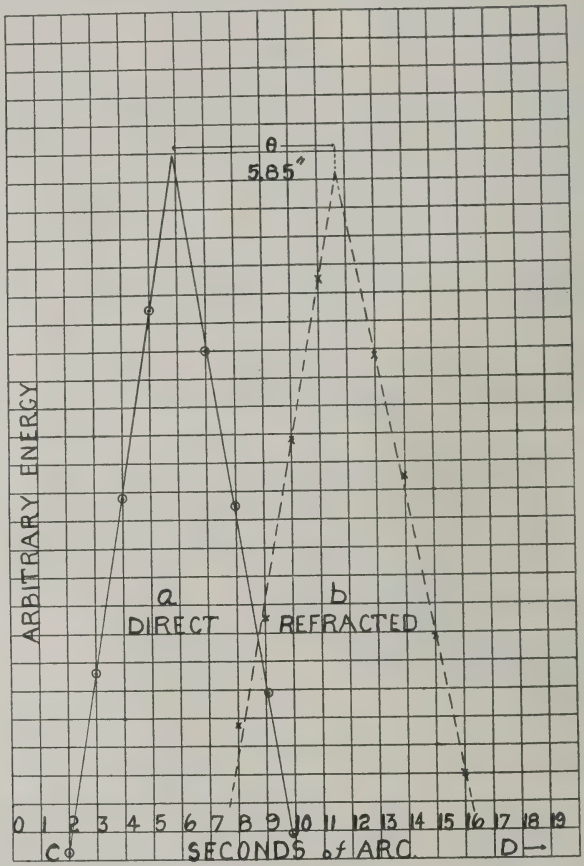

Fig. 2. Specimen curves showing the refraction in an aluminum prism.

The prism *P* in which refraction is to be measured is mounted on a carriage with a fine screw so that it may be run in and out of the path of the x-ray beam as desired. When the prism is in the path of the beam, the ray is refracted through an angle θ as shown. Crystal B is now rotated to reflect this refracted beam. A new rocking curve is obtained. The angular distance of the peak of this curve is equal to θ, the angle of refraction. The great advantage of the double x-ray spectrometer over the single is that the unequal absorption of the rays in the prism does not affect the position of the peak of the curves at all. This was directly tested by experiment. A piece of lead with a flat edge (not a prism) was mounted in place of the prism. When this piece of lead was pushed partially across the beam, the rocking curve was diminished in intensity, but the position of the peak was not altered.

Specimen curves for refraction in an aluminum prism are given in Fig. 2. Curve *a* was obtained with the direct beam *a* (Fig. 1) and curve *b* with the refracted beam *b*. Measurements were made for two frequencies, Mo Kα (λ.7078) and Cu Kα (λ1.537). The refracting angle R of the prism was 166° in case of λ.7078 and was 116° in case of λ1.537.

When the prism is symmetrically placed (position of minimum deviation) the index of refraction μ may be expressed by

$$\mu=1-\delta\ ;\ \delta=-\theta/2\tan\tfrac{1}{2}R$$

The sign of θ is negative for bending in the direction indicated in the figure.

The results obtained are given in the table.

λ	R	θ (obs)	Mean θ	$\delta\times10^{-6}$ (obs)	$\delta\times10^{-6}$ (calc)
.7078	166°	5.85″ 5.46 5.75 5.50 5.55	5.62″	1.68	1.77
1.537	116°	5.40 5.60 5.60	5.53″	8.4	8.36

The last column of the table gives the values of δ computed from the Lorentz dispersion formula. In the case of the radiation here used, the frequency is so far removed from the natural resonance frequencies of the aluminum atom that the simplified form

$$\delta=\frac{e^2}{2\pi m}\frac{1}{V^2},$$

was used for the computations.

The accuracy obtained in these measurements is well within ±5 percent. This accuracy might be increased by repeated measurements and in particular by maintaining constant temperature.

It was found that the position of the peaks of the curves often shifted during the course of a run. It was observed that the temperature also changed at the same time. On those occasions when the temperature was practically constant the shift was quite small. This shift apparently arises from an unequal expansion or contraction of the various parts of the apparatus, particularly the parts of the mechanism operating crystal B. Another source of error was the measurement of the angle R of the prism and the placing of it in a symmetrical position.

Phoenix Physical Laboratory,
Columbia University,
October 20, 1925.

PHYSICAL REVIEW JANUARY, 1926 VOL. 27

THE ABSORPTION SPECTRA OF THE VAPORS OF ALUMINUM, GALLIUM, INDIUM AND THALLIUM IN THE ULTRAVIOLET

By John G. Frayne and Alpheus W. Smith

Abstract

(1) *Absorption in heated vapors.* The metals were vaporized in a graphite tube 15 cm long heated with an oxyacetylene torch to temperatures up to 2000°C. A tungsten under-water condensed spark provided a continuous spectrum. *Aluminum.* At about 1200°C the first 7 pairs of the first subordinate series were absorbed. The relative intensities differ from what might be expected from the Bohr theory standpoint. No absorption was observed for the second subordinate series. *Gallium.* At a temperature of about 1500°C, 17 prominent lines appeared, including the first 4 pairs of the first and second subordinate series and the 5th term of the $2p_1-ms$ series. *Indium.* At a temperature of about 1200°C, 18 lines appeared, including the first 3 pairs of the first subordinate series, the first 5 pairs of the second subordinate series and the 4th term of the $2p_1-md$ series. *Thallium.* At 400°C, 4 lines of the $2p_2-ms$ and 4 of the $2p_2-md$ series appeared, widening into bands with increasing temperature. At 800°C, lines from the $2p_1$ level appeared as fine absorption lines. These results verify those of Grotrian. (2) *Absorption in the arc.* A bead of the metal was placed in a crater. *Aluminum.* In a 15 amp. arc the lines of the $2p_2-md$ and $2p_1-md$ ($m=5$ to 11) were completely absorbed. *Indium.* Besides the resonance lines $2p_2-2s$ and $2p_2-3d$, the lines $2p_1-2s$ and $2p_2-3d$ were completely absorbed. (3) *Relative behavior of lines from $2p_1$ and $2p_2$ levels.* The lines for the $2p_1$ level for gallium and indium are as readily absorbed as those for the $2p_2$ level and therefore may also be resonance lines.

Introduction

INVESTIGATION of the absorption spectra of aluminum and thallium vapors has been made by McLennan, Young and Ireton.[1] Using the method of arc reversals they found band absorption corresponding to some of the higher members of the $2p_2-ms$ and $2p_2-md$ series. Their results will be discussed below. Grotrian[2] found the first pair of the first and second subordinate series in gallium vapor completely absorbed. In a previous paper[3] he tells of having found several members of the first and second subordinate series absorbed in the vapors of indium and thallium. He used the method of passing a continuous ultraviolet spectrum through the vapor of the metal in an evacuated quartz tube. He was limited to temperatures of 1200°C and found few lines below 2400A. In a recent paper Narayan, Gunnayya and Rao[4] found band and line absorption in thallium vapor corresponding to several arc lines, including 3776A ($2p_2-2s$). Guthrie[5] and later Wood and Guthrie[6] made investigations of absorption in thallium vapor. Uhler and Tanch[7] found the lines 4511A ($2p_1-2s$) and 4101A ($2p_2-2s$) absorbed in indium vapor.

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[1] McLennan, Young and Ireton, Roy. Soc. Can. Proc., **13,** 9 (1919).

[2] Grotrian, Zeits. f. Physik **18,** 169 (1923).

[3] Grotrian, Zeits. f. Physik **12,** 218 (1922).

The present investigation was undertaken with a view to extending Grotrian's work to aluminum. Further, since the method described below made it possible to use temperatures as high as 2000°C, it was thought that new information could be obtained for the vapors of gallium, indium and thallium. It was also thought that further study of absorption in this group might help put a more satisfactory construction on the real meaning of the $2p_1$ level. At the present time it is considered a metastable level, while the $2p_2$ level is chosen as the stable orbit. There is very little experimental evidence for such a distinction, as direct resonance measurements have only been reported on thallium. It is a well known fact that resonance lines are readily absorbed in the normal vapor of the element, but the elements of this group not only have their resonance lines but also lines from the $2p_1$ level appear as absorption lines. The difference $2p_2-2p_1$ is small for aluminum, about .10 volt, increasing to about .96 volt in thallium. It is true that Mohler and Ruark[8] found a resonance potential of .9 volt in thallium vapor and Jarvis[9] has found a similar potential of .3 volt in gallium vapor. Grotrian found that absorption of lines from the $2p_2$ level took place at a lower temperature than from the $2p_1$ level, the temperature difference increasing from about 100°C in gallium to about 400°C in thallium. However, the fact that he did find lines from the $2p_1$ level strongly absorbed, seemed to indicate that they might be placed in the same category as those from the $2p_2$ level.

EXPERIMENTAL PROCEDURE

The metal under investigation was placed in a graphite tube 15 cm long open at both ends. An oxyacetylene torch was used as the source of heat. This method has been already described by Zumstein[10] who used it in a study of the absorption spectra of copper, silver and gold. In the case of aluminum and thallium it was found necessary to pass a stream of nitrogen over the metal to prevent oxidation. At very high temperatures the aluminum combined with the nitrogen, making it difficult to secure sufficiently dense vapor to show absorption.

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[4] Narayan, Gunnayya and Rao, Roy. Soc. Proc. **106**, 596 (1924).

[5] Guthrie, Dissertation (1908).

[6] Wood and Guthrie, Astrophys. J. **29**, 211 (1909).

[7] Uhler and Tanch, Astrophys. J. **55**, 291 (1922).

[8] Mohler and Ruark, J.O.S.A. **7**, 819 (1923).

[9] Paper not yet published.

[10] Zumstein, Phys. Rev. **25**, 523 (1925).

The continuous ultraviolet spectrum was produced by a condensed spark between tungsten electrodes under water. The spark circuit was similar to that described by Hulburt[11] with the exception that the auxiliary gap was an ordinary air gap with an air blast between the electrodes. This proved to be a very satisfactory arrangement, giving a continuous spectrum between 8000A and 2000A. A Féry type spectrograph was used throughout the work.

On account of the rapidity with which the graphite tube heated it was found impossible to take observations at temperatures which differed by less than 50°C.

EXPERIMENTAL RESULTS

Aluminum. Several absorption lines appeared about 1200°C. They were found to correspond to well defined arc lines (see Table I). The first six pairs of the first subordinate series were absorbed, the absorption being more prominent in the shorter wave-lengths. The line 3092A ($2p_1-3d$) was more strongly absorbed than 3082A ($2p_2-3d$). Neither the lines 3962A ($2p_1-2s$) and 3944A ($2p_2-2s$) nor any other lines of the second subordinate series were absorbed.

TABLE I

Absorption spectrum of aluminum vapor

	$\nu=2p_2-md$		*$\nu=2p_1-md$
m	λ(in I.A.)	m	λ(in I.A.)
3	3082.16	3	3092.84
4	2567.997	4	2575.411
5	2367.064	5	2373.360
6	2263.453	6	2269.212
7	2204.627	7	2210.046
8	2168.805	8	2174.028
9	2145.390	9	2150.59
†10	2129.44	†10	2134.70
†11	2118.52	†11	2123.38

* New absorption lines.
† Absorbed in the arc.

The arc reversal method also was used to detect absorption. A small bead of the metal was placed in the crater of the positive carbon and vaporised in a 10 ampere arc. Some of the spectrograms showed complete absorption of five pairs of the first subordinate series, beginning with the fourth pair. In addition, narrow reversals were observed in the second and third pair as well as in the first pair of the second subordinate series. When a 15 ampere arc was used absorption was extended to the third pair of the first subordinate series.

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[11] Hulburt, Phys. Rev. **24,** 129 (1924).

Gallium. One gram of gallium gave sufficient vapor for absorption when heated to a temperature of about 1500°C. The first four lines of the $2p_2-ms$ and $2p_2-md$ series were strongly absorbed. In addition, the first five lines of the $2p_1-ms$ and $2p_1-md$ series were absorbed. Band absorption occurred between 2620 and 2480A. This band became more pronounced at higher temperatures. The wave-lengths of the gallium lines given in Table II are taken from the Astrophysical Journal[6]

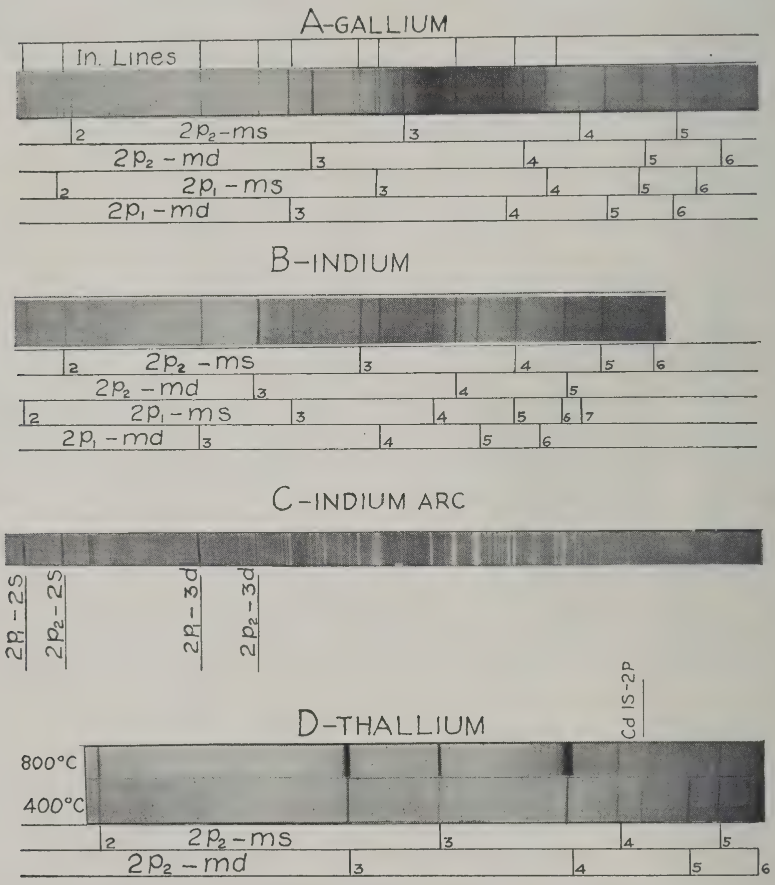

Plate I

of May, 1922. Plate IA is a reproduction of one of the spectrograms taken with this vapor.

In addition to the gallium lines there appeared as impurities the indium lines $2p_2-ms$ ($m=2$ to 4), $2p_2-md$, ($m=3$ to 5), $2p_1-ms$ ($m=2$ and 3) and $2p_1-md$ ($m=2$ and 3).

TABLE II

Absorption spectrum of gallium vapor

m	$\nu=2p_2-ms$ λ(in I.A.)	m	$\nu=2p_2-md$ λ(in I.A.)
2	4032.975	3	2874.24
*3	2659.873	*4	2450.078
*4	2371.325	*5	2294.202
*5	2255.034	*6	2218.039
m	$\nu=2p_1-ms$ λ(in I.A.)	m	$\nu=2p_1-md$ λ(in I.A.)
2	4172.06	3	2944.175
*3	2719.66	*4	2500.714
*4	2418.699	*5	2338.596
*5	2297.869	*6	2259.227
*6	2236.103		

* New absorption lines.

Indium. The lines absorbed in indium vapor are given in Table III. The first three lines of the $2p_2-ms$ and the first four of the $2p_2-md$ series

TABLE III

Absorption spectrum of indium vapor

m	$\nu=2p_2-ms$ λ(in I.A.)	m	$\nu=2p_2-md$ λ(in I.A.)
2	4101.764	3	3039.356
3	2753.889	4	2560.157
4	2460.079	5	2389.543
5	2340.191	12?	2181.70
*6	2278.20		
m	$\nu=2p_1-ms$ λ(in I.A.)	m	$\nu=2p_1-md$ λ(in I.A.)
2	4511.38	3	3258.565
3	2932.633	4	2713.932
4	2601.756	5	2522.854
5	2468.12	6	2430.70
6	2399.25		

* New absorption lines.

were strongly absorbed. In addition the first five members of the $2p_1-ms$ and $2p_1-md$ series were absorbed. A line corresponding to the emission line 2181A was absorbed. This may be $2p_2-12s$ but as this leaves the members of the series from $m=6$ to $m=11$ missing, the line is probably due to an impurity. All of the absorption lines occurred on every picture. Plate IB is a reproduction of a spectrogram taken at a temperature of about 1200°C. The emission spectrum of indium is reproduced in Plate IC. It will be noted that the lines $2p_2-2s$, $2p_1-2s$, $2p_2-3d$ and $2p_1-3d$ were completely absorbed in the arc. Aluminum emission lines were prominent in the arc but none appeared to be absorbed.

Thallium. Grotrian's observation that there was a 400°C difference between the appearance of lines from the $2p_1$ and $2p_2$ levels was verified in this investigation. The lines of the series $2p_2-ms$ ($m=2$ to 5) and $2p_2-md$ ($m=3$ to 6) appeared as fine absorption lines about 400°C. As the temperature increased these lines widened into bands extending asymmetrically toward the red. At 1200°C the lines $2p_2-2s$ and $2p_2-3d$ widened into bands of approximately 50A, while 2379A ($2p_2-4d$) extended about 38A. This latter line was the only one observed by Wood and Guthrie.[6]

TABLE IV

Absorption spectrum of thallium vapor

m	$\nu=2p_2-ms$ λ(in I.A.)	m	$\nu=2p_2-md$ λ(in I.A.)
2	3775.72	3	2767.87
3	2580.14	4	2379.58
4	2315.93	5	2237.84
5	2207.06	*6	2168.61
m	$\nu=2p_1-ms$ λ(in I.A.)	m	$\nu=2p_1-md$ λ(in I.A.)
2	5350.46	3	3529.43 3519.24
3	3229.75	4	2921.52 2918.32
4	2826.16	5	2710.67
5	2665.57	6	2609.77
6	2585.59	7	2552.53
7	2538.18	8	2517.41
8	2507.94	9	2493.91
9	2487.48	10	2477.49
10	2472.57	11	2465.46
11	2461.93	12	2456.45
		13	2449.49
		14	2443.92
		15	2439.50
		16	2435.80
		17	2433.0

* New absorption lines.

At about 800°C the lines of the series $2p_1-ms$ and $2p_1-md$ appeared as fine absorption lines. These lines did not widen into bands as the temperature was raised. The complete list of lines absorbed in this vapor is given in Table IV. Plate ID shows the lines from the $2p_2$ level only.

Discussion

The appearance of the aluminum lines is not what one would expect from the Bohr theory standpoint. In the first place, the resonance line 3944A ($2p_2-2s$) failed to appear as an absorption line. Secondly, the resonance line 3082A ($2p_2-3d$) appears only as a very faint absorption line, while the line 3092A ($2p_1-3d$) was much more prominent. Finally, the higher members of the series showed stronger absorption than those of longer wave-length. This latter point was also noted by McLennan, Young and Ireton,[1] who studied the absorption spectra by the arc reversal method. They found band absorption corresponding to lines of the $2p_2-ms$ ($m=4.5$ to 8.5) and $2p_2-md$ ($m=6$ to 14) series. They found no absorption of any lines from the $2p_1$ level.

The work of Grotrian[2] with gallium vapor was verified and thirteen new absorption lines discovered. He had found only the lines $2p_2-2s$, $2p_1-2s$, $2p_2-3d$, and $2p_1-3d$. The results of this investigation showed that lines from the $2p_1$ level were just as readily absorbed as those from the $2p_2$ level and that the term *resonance* might be equally applied to any line.

All of the lines found absorbed in indium vapor by Grotrian[3] were obtained on the spectrograms. In addition, the fifth member of the series $2p_2-ms$ (2278A) was strongly absorbed. The complete absorption of $2p_2-2s$, $2p_2-3d$, $2p_1-2s$ and $2p_1-3d$ points strongly to the suggestion that the latter pair might be considered in the same category as the former, which are recognised resonance lines. It is of interest to note that Uhler and Tanch[7] observed only 4511A ($2p_1-2s$) and 4101A ($2p_2-2s$) absorbed in indium vapor.

The results obtained in thallium vapor clearly differentiate between the $2p_2$ and $2p_1$ levels in this atom. The lines of the $2p_2-ms$ and $2p_2-md$ series appear without any of the lines of the $2p_1-ms$ or $2p_1-md$ series. Further, the lines from the $2p_2$ level are radically different from those from the $2p_1$ level in that they widen out into bands with increasing temperature whereas the latter lines remain as fine absorption lines. Only one new line 2168A ($2p_2-6d$) was found in this investigation. McLennan, Young and Ireton[1] found absorption bands in thallium vapor, corresponding to the lines $2p_2-md$ ($m=6$ to 10) and $2p_2-ms$ ($m=5.5$ to 11.5). They failed to find any absorption of lines from the $2p_1$ level. They explained their failure to find 3776A ($2p_2-2s$) by suggesting that the presence of Hg vapor was necessary to cause absorption of this line. This investigation shows that temperature and density are the controlling factors in the production of lines in the absorption spectrum.

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POLARIZATION OF RADIATION EXCITED BY ELECTRON IMPACT[1]

By A. Ellett,[2] Paul D. Foote and F. L. Mohler

Abstract

Polarized radiation following electron impact.—If a unidirectional beam of electrons, of velocity slightly in excess of the resonance potential, is projected through a vapor at a very low pressure so that effects due to atomic collision and resonance radiation are negligible, and in the absence of an applied field and resulting Larmor precession, there is reason to suspect that the radiation emitted perpendicular to the electron beam should be partially polarized, especially for lines corresponding to $\Delta j=1$.

Polarization in mercury and sodium vapor.—Experiment showed a polarization of about 30 percent for λ2537 with the greatest intensity of the electrical vibration having a direction perpendicular to the electron beam. No polarization was detected for the unresolved sodium D-lines, confirming the recent observation of Kossel and Gerthsen.

Polarization in mercury with field of 3 gauss.—A field parallel to the electron beam produced no effect. With the field perpendicular to the beam the radiation along the field was unpolarized while that perpendicular to the field was reduced in polarization to 13 percent. These results suggest that the atom radiates with the same distribution of polarization and intensity as in zero field but with the atom rotated through an angle determined by the time of excitation and the precessional velocity.

In the complete absence of an electric or magnetic field, the atoms of a gas at very low pressure are oriented at random. Let j_0 represent the number of units $(h/2\pi)$ of angular momentum characterizing each atom in the normal state. The effect of an inelastic impact with an electron is the production of an atom in an excited state having an increased amount of energy and an angular momentum j. In collisions at a velocity only slightly greater than that corresponding to the resonance potential, the final velocity of the electron is practically zero. Under these conditions it would appear that the vector representing the angular momentum transferred to the atom should be directed perpendicularly to the velocity of the electron before the collision.

Let us consider the case when the atom absorbs one unit of angular momentum $(j=j_0+1)$ which is subsequently radiated as a quantum of circularly polarized light. The axis of the circular vibration coincides in direction with j. For a uniform distribution of the j_0 vectors the statistical distribution of the j vectors, following collision with a unidirectional, univelocity beam of electrons, is readily obtained from simple geometrical relations. The j axis of any atom should remain fixed in direction since the assumption of no external field precludes precession during the time of excitation. The circular vibration emitted, as viewed by an observer looking perpendicularly to the electron beam, appears in general elliptically polarized. The elliptical vibration may be resolved along the directions parallel and perpendicular to the beam and the sums $I_{\parallel}$ and $I_{\perp}$ of the corresponding intensities for the circularly polarized radiations from all of the atoms representing the various orientations of j, may be calculated. The following formula for the resulting polarization of the radiation is obtained in the above described manner.

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[1] Published by permission of the Director of the National Bureau of Standards of the U. S. Department of Commerce.

[2] National Research Fellow.

$$\text{Polarization} = P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} = \frac{3(1 - j_0^2/j^2)}{9 - j_0^2/j^2}. \tag{1}$$

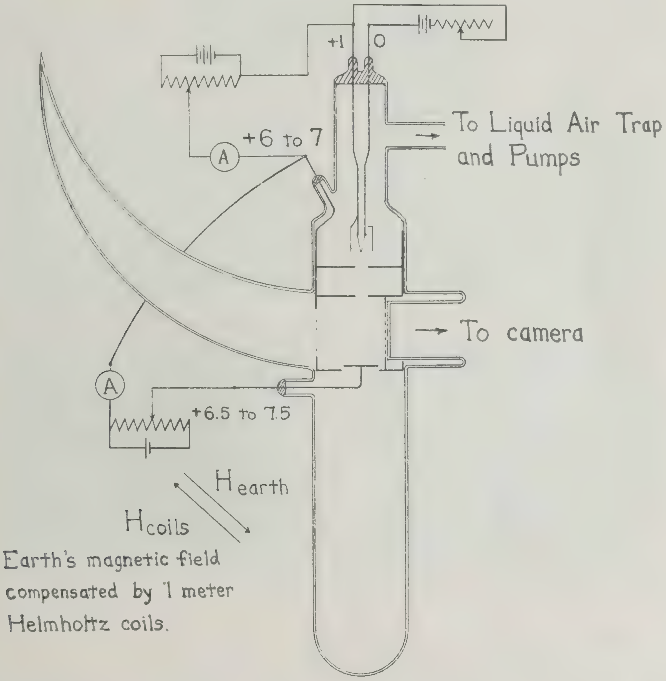
The experiment therefore appeared to afford a direct means for differentiating between the three systems of inner quantum numbers proposed by Sommerfeld, Landé and Bohr. Thus for the λ2537 line of mercury, as shown in Table I, the assumption of 0, 1/2 and 1 unit of angular momentum for the normal state of the mercury atom leads to values of the polarization which are readily distinguishable experimentally. Unfortunately these considerations fail entirely to explain the results obtained.

TABLE I

Percent of polarization computed from Eq. (1)

j_0	j	$I_{\parallel}/I_{\perp}$	P
0	1	2.00	33.3%
1/2	3/2	1.86	30
1	2	1.69	25.7
3/2	5/2	1.57	22.2

The experiment has been carried out with the λ2537 line of mercury and the sodium D-lines. Several different forms of discharge tube were employed, one found quite satisfactory for mercury being shown in Fig. 1. The hot wire source was a narrow platinum ribbon with a small spot of calcium-barium mixture directly opposite the pair of diaphragms of 3 mm opening. On making the focusing cylinder slightly positive relative to the activated spot on the platinum, a well defined beam of electrons could be projected into the observation chamber. By means of a quartz-glass re-entrant graded seal with a plane quartz window fused in the end, the scattering effect of the vapor surrounding the beam was reduced to a minimum. The chamber through which the beam passed was a platinum cylinder cut away in front for the observation window and in back so that the line of sight passed into the horn on the left. The entire tube was painted on the outside with lamp black, so that the horn made a very effective light trap for scattered radiation from the filament. The mercury vapor was at a pressure corresponding to −18°C, the lower part of the tube being immersed in an ice-salt bath. The vapor pressure on the mercury pump side was reduced by a liquid air trap. At this low mercury pressure the effect of secondary resonance radiation is practically negligible. For example, a beam of λ2537 radiation projected through a bulb of mercury vapor at −18°C is sharply defined, whereas at 0°C the scattered resonance radiation diffusely fills the bulb. The portions of the discharge chamber which were cut away for the observation window and horn were covered with a very coarse grid of two or three fine platinum wires to reduce electrostatic effects. The wires by the window served as fiducial marks defining different sections of the beam.



Earth's magnetic field compensated by 1 meter Helmholtz coils.

Fig. 1. Diagram of tube used for mercury vapor. The radiation produced by the beam of electrons was photographed through a quartz window by a camera with quartz lens and quartz Wollaston prism.

The potential required to excite the λ2537 line of mercury is 4.9 volts. However the next line $1S-2P$ is not produced below 6.67 volts, and since the quartz observing system was opaque to this line, fields up to 7 volts introduced no spectroscopic complications even in the excitation of λ2537 as a two-stage process. In general, the field employed was around 6 to 7 volts. A few exposures at somewhat lower voltage showed no pronounced differences. It was found necessary to use an additional electrode at the bottom of the cylinder at a potential a few tenths of a volt positive to the cylinder. In this way the effect of space charge in the beam was partially neutralized. With proper care the beam could be limited to the geometrical projection of the diaphragms and extended for about 2 cm, well past the observation window. The current represented by the beam was of the order 5 to 20 μ-amp.

The beam was photographed by means of a camera with a quartz objective. Between the objective and the tube was mounted a large quartz Wollaston prism so oriented that one image represented the intensity of the radiation polarized with the electric vector parallel to the beam and the other perpendicular. Plate I illustrates several typical exposures. The plates were photometered and a rough estimate of the intensity ratio was made on the assumption of a gamma value of 0.8 for the plate characteristic. This value is probably a fair assumption for λ2537 and the type of development employed, although of course it cannot be considered as quantitatively correct. Exposures were usually of about two hours. With mercury it was necessary to compensate for the earth's magnetic field by a pair of large Helmholtz coils since the vapor is extremely sensitive to the depolarizing action of a field. Lead-in wires for the filament current of about 5 amperes were twisted together and every precaution was taken to eliminate stray fields. Nothing but platinum was used in the construction of the discharge chamber and heavy platinum wires extended well back to the tungsten seals. These precautions were not necessary with sodium as is shown by the behavior of the resonance radiation in fields of one gauss or less. The usual high vacuum technique was employed. The tube was well baked at 360°C and, upon cooling, a drop of metal, after several distillations, was condensed in the bottom. The pressure on the fore-pump side was below that readable on a McLeod gage.

In order to be certain that the beam in mercury vapor represented true electron impacts and was not resonance radiation excited by the 2537 radiation produced between the filament and the diaphragm system, a weak magnetic field, perpendicular to the beam, was introduced by a second pair of Helmholtz coils. The beam was bent into a circular arc well out of the geometrical projection of the filament, proving the effect to be due to electrons.

Sodium. Since the beam in sodium is visible, photographic difficulties may be eliminated. The observing device consisted of a quartz wedge and nicol prism oriented for the production of fringes. No polarization was observed although a polarization of 2 percent could have been readily detected. It does not seem likely that the vapor pressure at 150°C was sufficient to have caused any depolarizing action by atomic collision. This experiment, which was made about a year ago, is an independent confirmation of the recent work by Kossel and Gerthsen.[3] They were led to the experiment by theoretical considerations quite different from those proposed above. Thus, according to their theory, the predicted

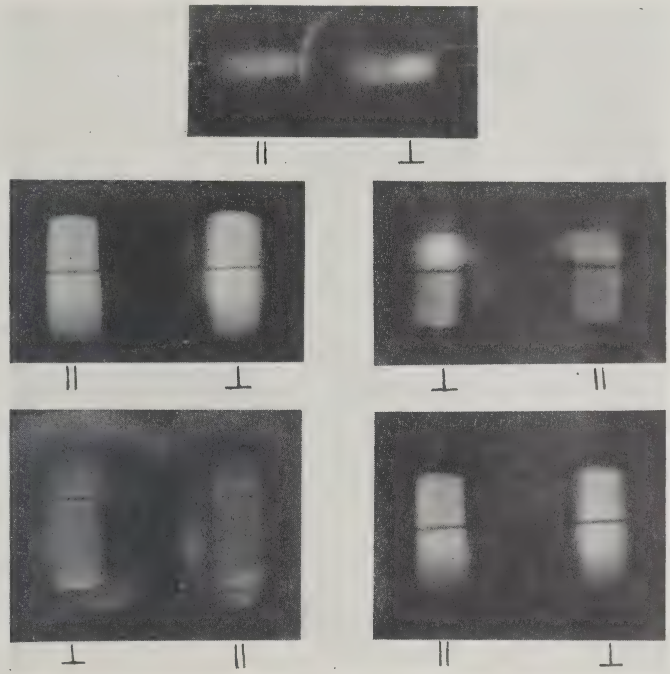


Plate 1. At −18°C the beam of λ2537 radiation from mercury vapor is sharply defined by the geometrical projection of the diaphrams limiting the beam of electrons. The width of the beam is about 3 mm. The ends of the beam are limited by the reentrant quartz tube and window. The component of the radiation polarized with the electrical vibration perpendicular to the electron beam is about twice as intense as the parallel component. Densitometer measurements on the original negatives were made at corresponding points of the two images as determined in reference to the wire marker reproduced as a black line. Since the difference in densities of the two images is only 0.2 to 0.3 the contrast is not striking. The upper photograph was made with a tube of different design and considerable scattered radiation from the hot wire is present.

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[3] Kossel and Gerthsen Ann. d. Physik, *77* pp. 273-86 (1925).

polarization is about 60 percent for 3 volt impacts. Since two lines are emitted, with $\Delta j=0$ and $\Delta j=1$ respectively, in the intensity ratio 1:2 we should expect, on the basis of Sommerfeld's quantum numbers, a polarization of 20 percent.

Mercury. With mercury vapor in the absence of any applied magnetic field, we find a polarization of about 30 percent with the greatest intensity of the electrical vibration having its direction perpendicular to that of the electron beam. The polarization therefore is in the opposite direction to that predicted by the theory outlined above and by that of Kossel and Gerthsen.

Using a uniform magnetic field of about 3 gauss, the following observations were made with mercury vapor. (1) A field parallel to the direction of motion of the electrons produced no effect perceptibly different from that without the field. (2) When the field was perpendicular to the direction of motion of the electrons, the radiation emitted along the field was unpolarized and that emitted perpendicular to both the electron beam and the field showed a polarization of 13 percent, the maximum intensity of the electric vibration being perpendicular to the electron beam.

These effects with the field are in the proper direction if the field produces a Larmor precession in the excited atom so that it radiates with the same distribution of polarization and intensity as it would in the absence of the field, but with the atom rotated through some angle determined by the time of excitation and the precessional velocity.

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PHOTO-IONIZATION AND RELATIVE ABSORPTION PROBABILITIES OF CAESIUM VAPOR*

By F. L. Mohler, Paul D. Foote and R. L. Chenault

Abstract

Measurement of photo-electric ionization in gases.—The method[1] depends upon the partial neutralization of the negative space charge around a hot wire cathode by the ions produced by radiation. The change in thermionic current is proportional to the product of the intensity of radiation, number of atoms of vapor per unit volume, the Einstein probability coefficient B_ν, a quantity R representing the number of electrons released by a single ion and certain numerical factors relating to the geometry of the apparatus. The magnitude of R is of the order 10^4 to 10^6 depending upon the vapor pressure and other characteristics of the tube. Under constant experimental conditions and when the change in current upon illumination is small compared to the total thermionic current, R assumes a definite fixed value. Hence the change in current per unit intensity at different frequencies gives relative values of B_ν.

Absorption probabilities.—The absorption probability coefficient of a caesium atom for wave-lengths shorter than the $1s$ limit λ3184 decreases much more rapidly with decreasing wave-length than follows from the λ^3 law of Milne or the λ^4 law of Kramers although the latter is satisfactory for x-ray absorption. The theory of Becker is in good agreement with the data for the range λ3050 to 2700. An empirical relation of the form $B_\nu = B_{\nu_1} e^{-a(\lambda_1-\lambda)}$ where $\lambda_1 = 3184$, appears to represent the experimental values throughout the observed range λ3184 to 2600. Vapor pressures investigated extended from 5 to 500 bars.

Photo-excitation.—Photosensitivity curves between λ3900 and the limit show that appreciable ionization is produced only at the wave-lengths corresponding to the principal series lines, the resolved effect of the individual lines being measurable from $1s-4p$ to $1s-9p$ with indications of further peaks, the definition of which was limited by the resolving power of the monochromator. The ionization is due to the production of excited atoms which are ionized by atomic collision. The relative magnitude of the photo-ionization at the different lines is in accord with the theory based upon the above hypothesis.

RECENTLY[1] two of the authors described a new method for detecting the photo-electric ionization of a gas, which was applied to the measurement of the photo-electric effect in caesium vapor. The vapor was contained in a two-electrode quartz tube. A hot wire cathode was enclosed by a cylindrical electrode having a gauze end through which the exciting radiation was transmitted. Conditions were adjusted to be such that the electron current without illumination was limited by space charge and the formation of ions by the radiation tended to break down the space charge and to produce an increase in thermionic current. This effect is greatly accentuated by the imprisonment of the ions, as a result of which a single ion may be responsible for the emission of 10^5 or more electrons. The photo-ionization of caesium vapor was found to be a maximum at the limit of the principal series, λ3184. Photosensitivity was also observed at longer wave-lengths which was attributed to the ionization by interatomic collision of excited atoms.

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* Published by permission of the Director of the National Bureau of Standards, U. S. Department of Commerce.

[1] Foote and Mohler, Phys. Rev. **26**, 195-207 (1925).

The present paper is a continuation of this work. The tube was operated at temperatures ranging from 130 to 230°C. With an applied voltage greater than the ionization potential, a current of about 10^{-2} amp. was obtained. As indicated by the voltage at which ionization occurred the actual potential difference was about 1 volt greater than the applied value. For the photo-ionization measurements the applied voltage was zero, and the current was 2×10^{-5} amp. which agrees with the value computed from the space charge equation when $V=1$ volt. The thermionic current was balanced out by a potentiometric circuit, and the galvanometer sensitivity was increased as desired for the radiation measurements. Under favorable conditions a sensitivity as high as 4×10^{-10} amp. per mm could be utilized. The increase in current due to the illumination, if small compared to the total thermionic emission, is proportional to the number of ions formed. With the potentiometric circuit, this increase in current is read directly from the galvanometer deflection.

The amalgam mirror of the Hilger quartz monochromator (aperture $F/7$ at λ3000) was replaced by a sputtered platinum surface, the reflection coefficient of which is known. As light sources were used a 400 watt concentrated filament Mazda lamp, a quartz mercury arc and a tungsten lamp with a quartz window, containing mercury vapor to suppress volatilization of the filament. The sources were focused on the entrance slit of the monochromator while no lens was employed between the exit slit and the ionization tube.

Galvanometer drift and slight changes in photosensitivity of the tube, in part due to temperature variation, were greatly reduced by using storage batteries for all the electrical circuits and by adjusting the currents several hours before obtaining the final measurements. Three galvanometer readings were observed at each monochromator setting, with the illumination on, off and on; a series of such measurements were made for a range of wave-lengths and then repeated in the reverse order. In general, slit widths of 0.005 inch were used with the Mazda lamp in the range λ3900 to 3100 while slits as wide as .04 inch were necessary with the quartz tungsten lamp at the shorter wave-lengths near λ2800.

Data showing the relative values of the ratio of photo-electric ionization to light intensity as a function of the wave-length are of especial interest in connection with the theoretical interpretation of ionization by radiation. Unfortunately the intensity of the radiation incident upon the ionization tube was insufficient for a direct evaluation by means of a thermopile. Dr. Coblentz very kindly made several thermopile measurements for us with the mercury arc as source, but only two or three of the strongest ultraviolet lines could be detected with certainty and the galvanometer deflections for these were less than 1 cm. Intensity values were therefore obtained by computation using the thermopile data merely as a check.

The radiation flux $J_\lambda \Delta\lambda$ with the tungsten-quartz lamp as source was assumed proportional to the intensity of a gray body at 3000°K, times the reflecting power of the platinum mirror, times the reciprocal of the dispersion factor of the monochromator. With the Mazda lamp, these values were further multiplied by the transmission coefficients of a sample of glass from a similar lamp.

EXPERIMENTAL DATA

Table I illustrates the experimental conditions under which the photo-ionization measurements have been made. The vapor pressures are computed from data by Langmuir and Kingdon.[2] At the four higher temperatures both tungsten lamps were employed and in the range λ3600 to 3100 readings were made with a 0.005 inch slit at 10A intervals. The Mazda lamp alone was used at the lower temperatures and fewer measurements were obtained.

TABLE I

Conditions for photo-ionization measurements
(Mazda lamp illumination)

Temp.	Pressure	Current at 3200A slit .01 inch	slit .005 inch
230°C	500 bars	19.5×10^{-8}amp.	4.7×10^{-8}amp.
202	170	24.2	5.7
182	74	....	2.9
162	29	9.0	2.2
149	15	6.7	...
134	9.7	4.2	...
128	5.0	1.6	...

Fig. 1 shows the photosensitivity, corrected for an equal energy spectrum, as a function of the wave-length, for the temperatures 182° and

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[2] Langmuir and Kingdon, Proc. Roy. Soc. **107A**, 61-79 (1925).

230°C. Table II gives some of the data for these curves as well as the relative values of the incident radiation flux. The last two columns tabulate the heights of the separate peaks in the curves of Fig. 1 from λ3880 to 3310 and the points on the continuous curve for shorter wave-lengths. These values are the directly determined means of the experimental data. There is a small but perceptible difference between the two curves of Fig. 1. Curves for 162° and 202° resemble closely that for 182°, as do also the less accurate data for the lower temperatures.

TABLE II

Photosensitivity and radiation flux for three sources

Flux for tungsten lamps relative to λ3184 as unity; mercury arc relative to λ3130 as unity. Data of Pflüger (Kayser's Handbuch) are chosen since they give the same ratio of intensities at 3130 and 2537 as our thermopile readings.

Source	Wave-length	Relative flux $J_\lambda \Delta\lambda$	Sensitivity for equal flux 182°C	Sensitivity for equal flux 230°C
Mazda lamp	3880A	28.0	....	.006
	3610	12.4	.038	.051
	3480	7.9	.069	.092
	3400	5.4	.092	.129
	3350	4.0	.156	.216
	3310	3.1	.20	.27
Quartz-tungsten lamp	3300	1.64	.18	.28
	3280	1.47	.25	.33
	3260	1.35	.37	.41
	3240	1.25	.54	.54
	3220	1.15	.76	.72
	3200	1.05	.93	.90
	3180	.95	1.00	.97
	3160	.85	.92	1.00
	3140	.79	.84	.97
	3120	.73	.73	.86
	3100	.67	.69	.75
	3060	.57	.52	.60
	3020	.47	.40	.48
	2980	.38	.33	.40
	2940	.32	.28	.33
	2900	.26	.19	.27
	2860	.21	.15	.21
	2820	.16	.14	.18
	2780	.13	.12	.17
Mercury arc		Thermopile		Pflgüer
	3130	1.0	.78	1.0
	3030	.27	.34	
	2970		(.35)	.3
	2650		.2	.2
	2537	.67	.42	.6

The measurements for wave-lengths greater than λ3300 may be shown to advantage on a much larger scale (Fig. 2). This figure includes data for 162° and 230°C and in the upper portion of the drawing a map of the principal series lines. The peaks coincide with the series lines within the precision of the monochromator setting; apparently the widths are

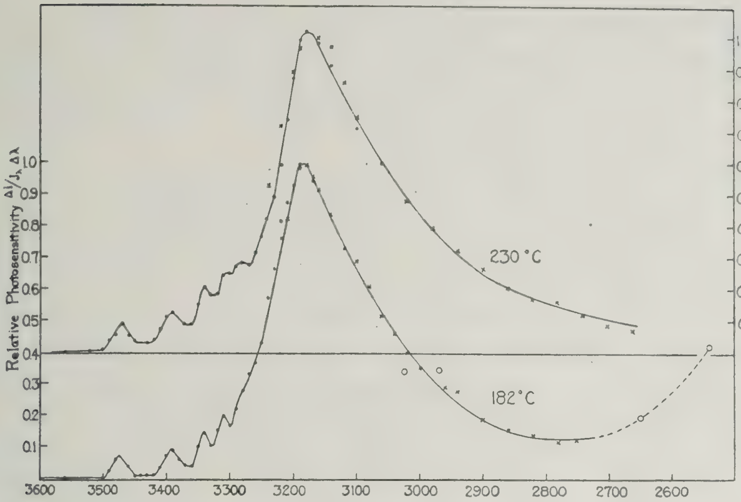

Fig. 1. Relative photosensitivity of caesium vapor corrected for an equal energy spectrum. The maximum sensitivity occurs at the limit 1*s* of the principal series.

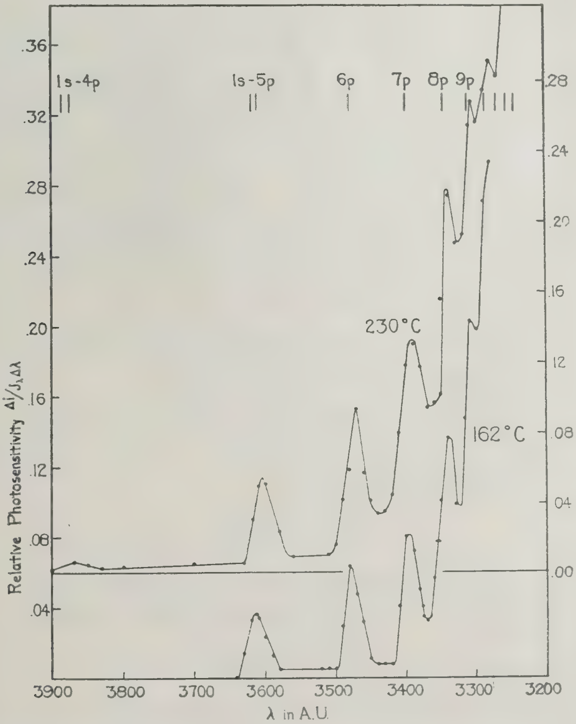

Fig. 2. Relative photosensitivity of caesium vapor on the long wave-length side of the photo-electric threshold. The peaks coinciding with the principal series lines are due to the ionization of excited atoms by interatomic collision.

determined by the resolving power of the instrument. Thus the observed effect for wave-lengths longer than λ3300 is largely if not entirely due to the separate lines. One may safely assume that in the range λ3300 to 3184 the curves show the unresolved effects of the closely-spaced higher members of the principal series.

INTERPRETATION OF EXPERIMENTAL DATA

Direct photo-electric ionization. Let us consider the numerical relationship involved between the observed photo-electric current and certain atomic properties of the vapor. If I_ν is the intensity of isotropic radiation of frequency ν, we may define the quantity B_ν such that $B_\nu I_\nu d\nu dt$ is the probability that an atom in the normal state absorbs a quantum of radiation and becomes ionized in the time dt under the influence of this radiation.[3] Let a beam of radiation having the solid angle $d\omega$ be incident at the angle ϑ on an element dS of the vapor surface. The amount of energy falling upon dS in the time dt is therefore $I_\nu d\nu \cos\vartheta dS\, d\omega\, dt$. If k_ν is the mass absorption coefficient and ρ is the vapor density, the fractional amount of energy absorbed by the thickness dx is $k_\nu \rho dx/\cos\vartheta$. Hence

$$\text{Energy absorbed in time } dt = I_\nu d\nu\, dS\, d\omega\, dt\, k_\nu \rho dx \qquad (1)$$

This energy is also given by the product of (the number of atoms in the volume under consideration) × (the probability of absorption by a single atom) × (the correction for lack of isotropism of the beam) × (the energy of a quantum) as follows.

$$\text{Energy absorbed in time } dt = N\, dS\, dx \cdot B_\nu I_\nu d\nu dt \cdot (d\omega/4\pi) \cdot h\nu \qquad (2)$$

where N is the number of atoms per cm^3. On equating (1) and (2) we find

$$k_\nu \rho / h\nu = B_\nu N/4\pi \qquad (3)$$

Eq. (3) therefore gives a simple relation between the mass absorption coefficient and the Einstein probability factor B_ν.

Let $E_\nu = J_\nu d\nu = J_\lambda d\lambda =$ the energy flux between ν and $\nu + d\nu$ in ergs per sec. per cm^2 surface of the vapor taken normal to the beam. Then at the depth x the flux is given by

$$E_\nu' = E_\nu e^{-k_\nu \rho x}. \qquad (4)$$

For the small values of $k_\nu \rho x$ concerned in the present work, on putting the energy absorbed $(E_\nu - E_\nu')$ equal to ΔE_ν this reduces to

$$\Delta E_\nu = E_\nu k_\nu \rho x. \qquad (5)$$

The number of quanta absorbed is $\Delta E_\nu / h\nu$ and if the absorption of each quantum results in the production of an ion, this is equal to the number of ions produced per second per cm^2 of cross-sectional beam area and depth x. The total number of ions n, produced in the ionization chamber of volume $w(=x\times$cross section of beam) is therefore

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[3] See Milne, Phil. Mag. **47**, 209 (1924).

$$n=E_\nu k_\nu \rho w/h\nu \tag{6}$$

Let $i=$number of electrons emitted by the hot wire per second when the current is limited by space charge, and $\Delta i=$increase in this number due to the presence of ions, then

$$\Delta i=Rn \tag{7}$$

where R by definition represents the number of electrons which a single ion is capable of releasing by partial neutralization of the negative space charge. The characteristics of this quantity will be considered below. On substituting the value of n from Eq. (6) and by use of Eq. (3) we finally obtain

$$\Delta i=(RE_\nu wN/4\pi)B_\nu. \tag{8}$$

The increase in current Δi, on illumination, is given by the galvanometer deflection. Theoretically E_ν could be evaluated absolutely by use of the spectrothermopile although with the sensitivity at our disposal the best that could be hoped for was a rough estimate of the energy over a very wide spectral range. Thus if R were known, an approximate estimate of B_ν in absolute value could be obtained. While this is a very indirect method of evaluating B_ν it would appear to offer greater possibilities than the direct determination of the absorption coefficient and the use of Eq. (3). For example Harrison's data[4] on sodium under dynamic equilibrium, as nearly as may be estimated from the tabulated measurements, indicate a mass absorption coefficient, on the short wave-length side near the limit, of $k_\nu=3\times 10^{-4}$ or an atomic coefficient $=k_\nu\rho/N=10^{-18}$. Since Harrison and Slater present evidence that with the rapidly distilling vapor at the high temperatures employed there are about 50 times as many diatomic molecules as atoms, the consideration of this coefficient as an atomic constant is, of course, questionable; however, it may indicate order of magnitude. The physical process occurring in photoelectric absorption near the limit is the same for all alkalies so that caesium should have an atomic absorption coefficient of the same order of magnitude as sodium. At the highest pressure we employed, 500 bars, an absorption coefficient of 10^{-18} would necessitate a tube 900 cm in length for an absorption of 50 percent. The experiment, therefore, is not promising for observations under static equilibrium, whereas, by the photo-electric method described, operation at much lower pressure, with a resulting increase in the relative concentration of monatomic vapor, is quite satisfactory.

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[4] Harrison, Phys. Rev. **24,** 474 (1924); Harrison and Slater, idem **26,** 176 (1925).

We have attempted to evaluate R the efficiency factor of the tube. Measurement of the current produced by illumination when the filament is not heated should give the ion current plus the photo-electric emission from the filament, the latter being slightly negative to the cylinder. It was hoped that from measurements at different pressures, the second factor could be eliminated, but the results were not sufficiently reproducible. The data indicate that R is greater than 10^4 at the highest pressure employed and may be as large as 10^6 at lower pressures.

Kingdon[5] used a tube especially designed for the determination of R and in certain cases observed values as great as 300 times the mobility ratio of ions to electrons at low pressure, corresponding to 10^5 for caesium. He also found that R was proportional to the $-2/3$ power of the pressure. Using data in Table I of our earlier paper, one finds that Δi is proportional to $p^{0.4}$, and remembering that N in Eq. (8) is proportional to p, this gives R as proportional to $p^{-0.6}$, in fair agreement with Kingdon. The factor R besides depending upon the general geometry of the apparatus involves the recombinations which occur between the ions and electrons. With the weak fields employed for our work, it is very sensitive to changes in applied potential or space charge as altered by varying the filament temperature. The space charge may be appreciably affected by intense illumination and the resulting production of ions, especially at the higher pressures. If however, the value of Δi is not greater than possibly 1 percent of the total thermionic current i, the direct proportionality between Δi and E_ν as a variable is quite accurately fulfilled; that is, R remains a constant. This relation was carefully checked by use of wire gauze absorption screens and all of the observations recorded in the present paper are within the prescribed limit. One must finally consider whether or not R depends upon the frequency ν. The tube is sensitive to the production of ions and insensitive to electrons. All the ions are of the same type regardless of the radiation by which they are produced. The photo-electrons to be sure are ejected with a velocity dependent upon ν, but especially when present to only 1 part in 10^7, in order of magnitude, of the normal thermionic current i it seems impossible that R may be affected by small changes in ν.

Hence, according to Eq. (8), for Δi small compared to i and with constant experimental conditions, i.e., vapor pressure, temperature, filament temperature and applied potential, Δi is directly proportional to $E_\nu B_\nu$. Since $E_\nu = J_\nu d\nu = J_\lambda d\lambda$ or, considering the finite slit width, since $E_\nu = J_\lambda \Delta\lambda$ we have

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[5] Kingdon, Phys. Rev. **21**, 408-18 (1923); our R is equivalent to Kingdon's α.

$$\Delta i = KJ_\lambda \Delta\lambda B_\nu \tag{9}$$

where K is a proportionality constant. The curves of Figs. 1 and 2 and the data in Table II represent relative values of $\Delta i/J_\lambda\Delta\lambda$ as a function of λ. Hence, the ordinates of the curves give the relative values of the probability coefficient B_ν for a ν value corresponding to the indicated λ. We believe that with especially designed apparatus the absolute values of B_ν may be obtained with some accuracy as indicated above, but for the present only relative values will be considered.

Since B_ν is an atomic constant, it should be independent of the pressure. This is qualitatively confirmed by the geometrical similarity of the two curves of Fig. 1 and several other curves not here reproduced. There are no data available in the literature for direct comparison. The lower curve shows an apparent increase in photosensitivity between λ2700 and 2500. The evidence is based chiefly on the measurements with the mercury line λ2537. Lawrence has suggested to us that this increase may arise from ionization of caesium molecules, an explanation consistent with his results for potassium vapor.[6] Another possibility is that merely a trace of mercury was present with the cycle of phenomena: absorption of λ2537; excited mercury atom; collision of the second type; highly excited caesium atom; completion of ionization by collision. While the usual precautions were taken to exclude mercury by baking the apparatus, etc., a small amount in the caesium could not have been completely removed by distillation. Spectroscopic examination of the vapor in a discharge at 10 volts failed to show any mercury lines, but prominent lines of rubidium and potassium were observed. These impurities could not have been present in a concentration sufficient to have affected our data. The caesium chloride from which the caesium was prepared by distillation in the presence of calcium was supposed to be fairly pure. Several fractional distillations in vacuum were made at low temperature which should have increased the purity since both potassium and rubidium have one fifth the vapor pressure of caesium at 250°C. Finally the percentage impurity present in the metal is reduced in the vapor by at least the factor 5 on account of the vapor pressure ratio. No evidence for either of these impurities was detected in the photosensitivity curves which, with an appreciable impurity, should have shown increased sensitivity at the corresponding principal series limits.

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[6] Lawrence, Phil. Mag. **50**, 345 (1925).

In the x-ray range B_ν is fairly well known empirically as a function of ν or of λ. Referred to a particular x-ray level it is a discontinuous function equal to zero for wave-lengths greater than the absorption limit and is approximately proportional to λ^4 for shorter wave-lengths. Various attempts have been made to derive theoretically the form of the B_ν curve, notably by Kramers,[7] Milne[8] and Becker.[9] For an isotropic radiation field they find the relation between the probability of absorption of a quantum $h\nu$, resulting in ionization, and the chance of recombination of an ion with an electron of velocity v where ν and v are related by the photo-electric equation

$$\tfrac{1}{2}mv^2 = h\nu - h\nu_1 \tag{10}$$

ν_1 being the limit of the absorption series. The chance of recombination may be expressed in terms of the "effective collision area" q for an encounter resulting in recombination. The general relation between B_ν and q is

$$B_\nu/q = (\nu-\nu_1)/\nu^3 \times \text{constant.} \tag{11}$$

By the introduction of rather speculative assumptions as to the law of recombination, the following results are obtained. Kramers finds B_ν proportional to ν^{-4} or to λ^4. Milne's work leads to a proportionality between B_ν and ν^{-3} or λ^3 in which he excludes its applicability to x-rays, although the argument for this is by no means apparent.[10] Becker derives the relation

$$B_\nu = \frac{1}{(\nu-\nu_1)\nu^3}\left[1 - \frac{(\nu-\nu_1)^2}{4\nu_1^2}\right] \times \text{constant.} \tag{12}$$

Eq. (12) is not applicable near the limit since it becomes infinite for $\nu=\nu_1$. Fig. 3 shows the form of these three theoretical relations, expressed by B_ν as a function of λ, together with our experimental values. The λ^3 and the λ^4 laws entirely fail in representing the data but satisfactory agreement with Becker's equation obtains in the range $\lambda 3050-2700$. An empirical relation of the form $B_\nu = B_{\nu_1} e^{-a(\lambda_1-\lambda)}$ where $\lambda_1 = 3184$, and B_{ν_1} is the value of B_ν at this wave-length, represents the observations in the range $\lambda 3184-2600$. If the data by Harrison on the absorption of the mixture of sodium atoms and molecules at high pressure are converted into relative B_ν values by use of Eq. (3) the general shape of curve obtained resembles our measurements, certainly in preference to a third or fourth power relation.

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[7] Kramers, Phil. Mag. **46**, 836-71 (1923).

[8] Milne, Phil. Mag. **47**, 209-41 (1924).

[9] Becker, Zeits. f. Phys. **18**, 325-43 (1923).

[10] Milne loc cit. p. 229.

For the spectral range λ3050 to 2700 the second term in brackets in Eq. (12) is negligible. Hence on combining this expression with Eq. (11) one finds

$$q=\frac{\nu^3}{\nu-\nu_1}B_\nu\times\text{const.}=\frac{\text{const.}}{(\nu-\nu_1)^2}$$

and by Eq. (10)

$$q=\text{const.}/v^4=\text{const.}/V^2 \tag{13}$$

where V represents the velocity of an electron expressed in volts. This law is consistent with our observations between 0.15 and 0.5 volt. For lower voltages there is a wide departure. Eq. (13) is the Thomson law of recombination and cannot apply at low speeds since q must satisfy the condition that in Eq. (11) B_ν is finite when $\nu=\nu_1$.

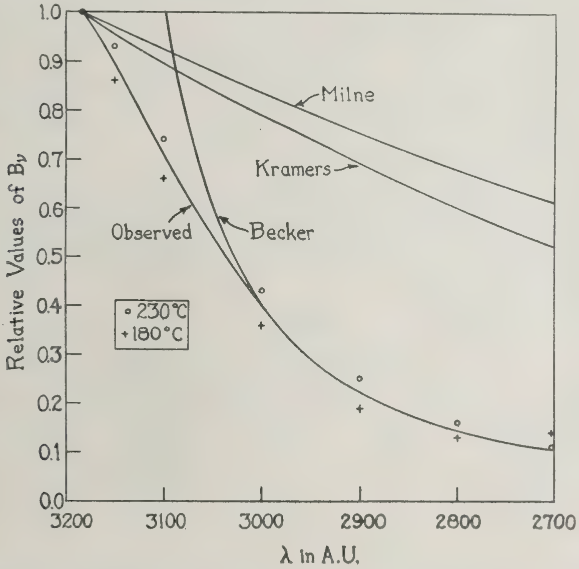

Fig. 3. Observed absorption probability of the caesium atom as a function of λ and graphs of the theoretical relations derived by Milne, Kramers and Becker.

Photo-ionization by line absorption. The observed relative sensitivity for direct photo-electric ionization, on the short wave-length side of the limit, and indirect ionization at points corresponding to the principal series lines depends upon the resolution of the monochromator. If both entrance and exit openings are doubled, the width of spectrum transmitted and the energy flux at each point in the exit slit are approximately doubled. When the vapor absorbs a continuous band the energy available for photo-electric ionization is therefore multiplied by four. At λ3200, the principal series lines are so close together that roughly the absorption may be considered as continuous so that even here the four-fold change in sensitivity should be expected, as illustrated by the data in Table I. If the absorption line is narrow compared to the slit width and lies in the spectral region corresponding to the first few terms of the principal series where the monochromator may differentiate definitely between the effects due to the adjacent members, doubling both slits approximately doubles the sensitivity of the tube. That is, the increase in heterochromatism of the beam produces no effect since the absorption is selective. At the low pressures employed, the absorption lines are very narrow so by decreasing the slit width the ordinates on the long wave-length side of a photosensitivity curve, such as Fig. 1, may be increased relative to those on the short wave-length side. Theoretically this process could be continued until the slits and absorption lines were of comparable width. The significance of the curve in the transitional region between these two conditions is therefore quite indefinite.

Table III shows the relative sensitivity of the tube at wave-lengths corresponding to the six principal series lines $1s-4p$ to $1s-9p$, a spectral region, except possibly for the last line, which is outside of the transition stage mentioned above. The small corrections for dispersion of the monochromator have been removed from these values since the lines are narrow compared with the slit width. The numbers represent the relative heights of the observed peaks measured from the axis of zero sensitivity thus neglecting the small effect due to scattered radiation. While the lines are somewhat superposed, the sensitivity contributed by one line to the *observed peak* of a neighboring line does not become appreciable for wave-lengths greater than $1s-9p$. Some change in relative sensitivity at the peaks for different temperatures is indicated but for the

TABLE III

Photo-ionization by line absorption
(Relative sensitivity at absorption lines)

Temp.	$1s-4p$ (3880)	$1s-5p$ (3611)	$1s-6p$ (3480)	$1s-7p$ (3400)	$1s-8p$ (3350)	$1s-9p$ (3314)
230°C	.1	.62	1.0	1.30	2.08	2.5
203	.12	.64	1.0	1.38	1.90	2.5
182		.62	1.0	1.24	2.00	2.5
161		.66	1.0	1.23	2.00	2.8
149		.70	1.0	1.36	1.98	3.3
134		.60	1.0	1.43	1.67	2.6
128		.60	1.0	1.15	1.32	1.9

pressure range represented, 5 to 500 bars, it is surprising to find the data so nearly constant.

The observed photo-ionization arises from a type of multiple excitation. From the data presented in the first paper, it was concluded that atoms in an excited state having a low ionization potential as a result of line absorption, may be ionized by collision with other atoms. The values given in Table III permit an extension of this idea. The probability of ionization depends upon at least three factors: (1) probability of absorption, (2) chance that the kinetic energy of collision is sufficient to complete ionization and (3) chance that the excited state persists or is passed on by resonance until collision occurs.

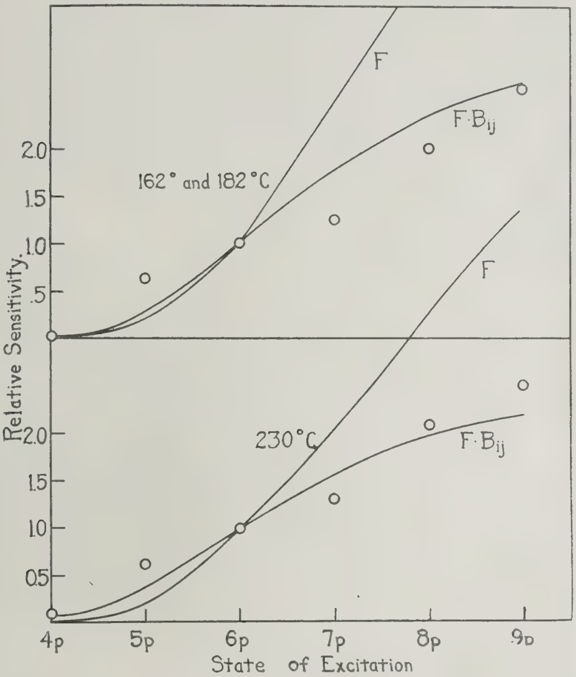

Fig. 4. Observed photosensitivity, represented by circles, of the caesium atom on the long wave-length side of the 1*s* limit. The curve FB_{ij}, except for a small variable and unknown factor, is the probability for the occurrence of the physical process responsible for the sensitivity.

The first factor depends upon the probability B_{ij} that the atom in the normal state i absorbs a quantum and passes over to the state j. These probability factors are unknown for the caesium lines here concerned but Ladenburg[11] has shown that the principal series of the alkalies are much alike in this respect so we may use the data by Harrison[12] for the relative probabilities in sodium. The chance of ionization by collision from an excited *mp* state may be estimated roughly by use of the kinetic gas theory. In the earlier paper this factor was designated by F. The third probability is unknown but is nearly unity at higher pressures. Fig. 4 shows the relative, observed photosensitivity at the successive lines, plotted as circles, and relative values of F and FB_{ij} for two temperature ranges. Qualitatively the agreement is excellent.

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[11] Ladenburg, Zeits. f. Phys. **4**, 451-68 (1921).

It is of interest that these experiments on the long wave-length side of the photo-electric limit yield a map of the principal series somewhat similar to an emission spectrum, yet no emission is taking place; in fact the sensitivity depends upon the suppression of the emission.

The authors desire to thank Dr. Sebastian Karrer of the Fixed Nitrogen Laboratory for lending them the quartz monochromator.

Bureau of Standards,
Washington, D. C.
October 5, 1925.

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[12] Harrison, Phys. Rev. **25**, 768-82 (1925).

PHYSICAL REVIEW JANUARY, 1926 VOL. 27

LAWS GOVERNING THE PULLING OF ELECTRONS OUT OF METALS BY INTENSE ELECTRICAL FIELDS

By R. A. Millikan and Carl F. Eyring

Abstract

Current from thoriated tungsten filaments in vacuum, due to radial fields of up to two million volts per cm.—Three filaments were tested, each .00123 cm in diam. and suspended under tension in the axis of a copper cylinder of 1.6 cm diam. From the dimensions, the radial field at the surface of the filament was 228 times the applied potential difference. The electron currents pulled from the tungsten by the high fields (field currents) rise steadily from 10^{-12} to 10^{-8} amp. as the field is increased from about 400 to 1100 kv/cm. In the dark, luminous spots were seen on the anode, indicating that these currents come from a few active surface spots. The field current (for a given voltage) depends on the value of the maximum field current previously drawn from it (conditioning current), being reversibly reproducible below the conditioning current. The higher the conditioning current, the lower the field current. A previous heating to high temperatures (2400°C) decreases the field current and also decreases the slope of the current-voltage curve. Both effects (current and heating) show fatigue. *Variation with temperature of the filament, to* 800°C. The field currents are completely independent of temperature up to 700°, but a temperature of 800° increases the currents due to a given field when this is sufficiently large, by a factor which is roughly independent of the current (10^{-8} to 10^{-4} amp.). *Electron theory.* In explanation of these results, it is suggested that the field currents are due to conduction electrons pulled from minute peaks on the surface, the fatigue effects of both current treatment and heat treatment being due to the rounding off of these peaks by positive ion bombardment or by temperature. Chemical changes may also alter the surface. The lack of dependence of field currents upon temperature furnishes strong evidence that most of the conduction electrons do not share in the energy of thermal agitation. The thermions, however, do share in this energy; they are presumably responsible for the Peltier and thermo-electric effects. In this theory it is assumed that conduction electrons follow the same sort of quantum laws in their escape from the solid as do atoms of a light element at temperatures far below the boiling point.

I. Introduction

THE experiments of Earhart,[1] Kinsley,[2] Hobbs,[3] Hoffman,[4] and Lilienfeld,[5] a previous investigation by one of us,[6] and the theoretical discussion of Schottky,[7] all indicate that electrons may be pulled out of metals by intense electrical fields. In particular the experiments of Hobbs, which were suggested by and carried out under the direction of one of the present authors, made possible the computations of the field strengths at which this effect begins to appear. Many years ago the first of us made these computations and then endeavored to check the values obtained by new experiments made with spherical electrodes about 1 mm apart in the highest obtainable vacuum. After continuing this investigation with many modifications intermittently for a considerable number of years it became evident that in a vacuum so high that the gas plays no further part in the discharge, the potential gradient at the metal surface necessary to obtain a discharge is exceedingly variable even for the same metal surface. The most recent of these results were published very briefly in 1920.[6] It was found that with clean untreated surfaces—two crossed tungsten wires, size No. 18, placed a small fraction of a millimeter apart—a first leak, as measured on a tilted electroscope, was obtained at a gradient of from 100,000 to 500,000 volts per centimeter. When heated to red heat and then cooled, these same surfaces gave a first leak at from 400,000 to 700,000 volts per centimeter. After heating to 2700°K the first leak was pushed up to 4,300,000 volts per centimeter and the first spark up to six million volts per centimeter. The present investigation is a continuation of this attempt to see just how far surface conditions control the field strength needed to pull electrons out of cold metals, and how "field-currents" depend upon field-strength, temperature, etc.

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[1] Earhart, Phil. Mag. **1,** 147 (1901); Phil. Mag. **16,** 147 (1908).

[2] Kinsley, Phil. Mag. **9,** 692 (1905).

[3] Hobbs, Phil. Mag. **10,** 617 (1905).

[4] Hoffman, Verh. d. Deutsch Phys. Ges. **12,** 880 (1910); Phys. Zeits. **11,** 961 (1910); Zeits. f. Physik **4,** 363 (1921); Phys. Zeits. **13,** 480, 1029 (1912); Ann. d. Physik **42,** 1196 (1913); **52,** 665 (1917).

[5] Lilienfeld, Akad. d. Wiss. Leipzig, Ber. (Math. Phys. Kl) **62,** 31 (1920); Verh. d. Deutsch Phys. Ges. P. **11** (1921); Phys. Zeits. **20,** 280 (1919); Phys. Zeits. **23,** 506 (1922).

[6] Millikan and Shackelford, Phys. Rev. **15,** 239 (1920).

II. Apparatus and Method

Since we wished to make the distance between the electrodes of the order of a centimeter it became necessary to design the apparatus in a manner such that the field intensity at the surface to be investigated would be very large *because of the small radius of curvature of the surface* and such advance as we have here made has been due primarily to this condition. Accordingly a tungsten wire of .00123 cm diameter was placed at the axis of a copper cylinder of 1.625 cm diameter. From these dimensions the field strength F at the surface of the wire becomes

$$F=228\ \phi$$

where ϕ is the difference in potential between the electrodes.

The tungsten wire W and the copper cylinder C were placed in a Pyrex glass tube as shown in Fig. 1. The wire is kept taut by a four-gram iron weight I, and is adjusted so as to be in the axis of the cylinder.

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[7] Schottky, Zeits. f. Physik **14,** 80 (1923).

Two leads are connected to either end of the fine wire and then brought through a seal in the upper part of the tube. It is thus possible to send a current through the tungsten wire and thereby to heat it to any desired temperature. When the wire is heated to temperatures over 1100°K the iron weight is lifted by means of an electromagnet, *E*. With this arrangement one may keep the wire taut at low temperatures and yet be insured against its breakage at high temperatures.

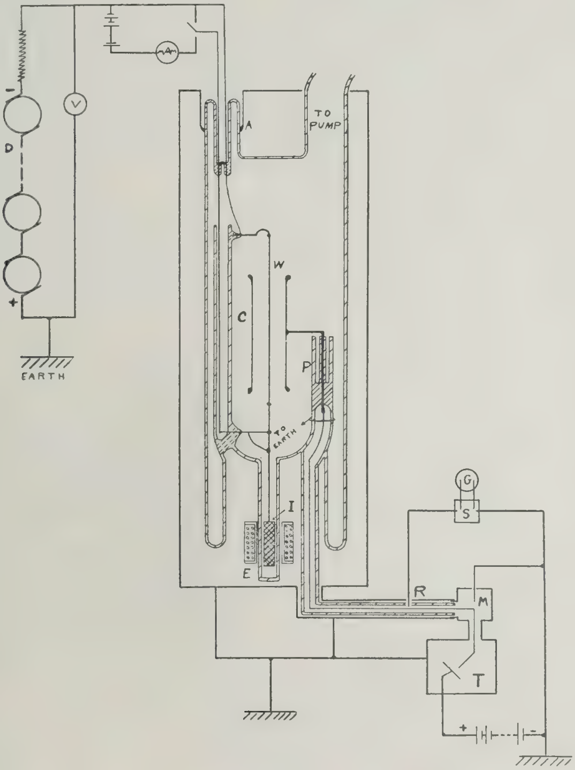

Fig. 1. Diagram of apparatus and electrical connections.

The cylinder is supported by a large tungsten wire that is sealed into the post *P*. This post has a glass sleeve to protect it from becoming coated with a deposit of copper when the cylinder is heated to bright redness in the process of denuding it of gases, otherwise the post might lose its insulating properties. An earthed guard ring is placed around the post *P* so that in case a charge should leak over the inside of the glass, none of it would reach the cylinder. The large tungsten wire passes through the seal in the post to the outside of the tube where it is joined to a copper wire leading to the tilted electroscope. A small glass tube is sealed to the main tube in such a manner as to enclose this conductor which is then electrically shielded by covering the glass with earthed tin-foil.

An electric heater surrounds the main glass tube. The metal cylinder on which the heating coils are wound is grounded and thus the heater serves as an electric shield for the tube. A grounded guard ring is placed at *A* to keep the outside of the tube from becoming charged when a high potential is applied.

Direct current generators are used as the source of high potential, the maximum voltage available being 12000 volts. In series with the generators is placed a resistance of a million ohms to protect the apparatus should a short circuit be established between the wire and the cylinder. A Max Kohl electrostatic voltmeter *V*, calibrated in place, is used to measure the potential applied between the wire and the cylinder. A tilted electroscope *T* and a galvanometer *G* provided with a variable shunt are used to measure the "field-current" between the wire and the cylinder. The wire to the galvanometer is disconnected at *R* when the tilted electroscope is being used.

After properly baking the tube and charcoal trap during exhaust, a pressure of less than 10^{-6} mm of mercury was obtained. The tube would stand over night with liquid air on charcoal and mercury vapor traps, and then show no measurable pressure on the McLeod gauge (reading to less than 10^{-5} mm), and when the pumps were running, as was always the case during observations, the pressure was certainly far below 10^{-6} though no attempt was made in these particular experiments to measure it accurately. However, with the use of high speed mercury pumps, wide openings, charcoal in liquid-air, and precautions for denuding, the vacua here used were presumably as high as can now be produced.

At the proper time in the investigation the cylinder was heated to cherry red for from eight to twelve minutes by electronic bombardment. The bombarding potential was 2,000 volts and the bombarding current 100 milliamperes. The filament used as the source of thermions is stretched in a series of zigzags around and within half a centimeter of the cylinder. This part of the apparatus is not shown in the figure.

If the wire is to be heated simultaneously with the application to it of a potential, the apparatus used to furnish and measure the heating current is placed on an insulated stand. Using data published by Langmuir[8] the temperature of the wire is obtained from the value of the current in the wire and its diameter.

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[8] Langmuir, Phys. Rev. **7**, 302 (1916).

Observations were taken on three specimens of thoriated tungsten wire. These pieces were from the same spool and, as explained above, had a diameter of .00123 cm. When a new wire was introduced the tube was opened up, the wire supplied, and the tube sealed up again.

III. Results

(a) *The rapid rise of "field-current" with increasing potential gradient and the reversibility of the process.* The wires will be numbered I, II, III, the numbers indicating the order in which they were investigated. Fig. 2 presents the data obtained for wire I which had received no heat treatment other than that involved in baking out the tube, but which had been "conditioned," as explained below, by a .42 milliampere "field-current" (the current between the wire and the cylinder due to the pulling of electrons from the tungsten wire by the field alone). The figure clearly shows that *for a clean "field-current-conditioned" tungsten surface, but not heat-treated, the "field-current" increases more than ten-million-fold with a threefold increase of potential gradient,* i.e. *a gradient varying between .40 × 10^6 and 1.13 × 10^6 Volt cm. These data further show that for "field-currents" lower than the current which conditioned the surface the process is quite accurately reversible.*

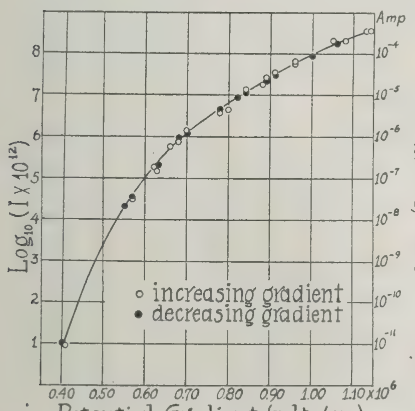

Fig. 2

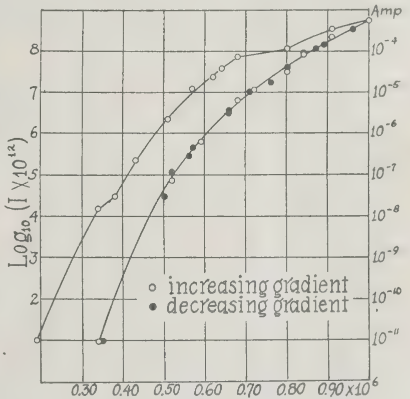

Fig. 3

Fig. 2. Variation of the logarithm of the "field-current" with potential gradient, for wire I, "conditioned" by a .42 m.a. "field-current."

Fig. 3. Variation of the logarithm of the "field-current" with potential gradient, for wire II, during and after "conditioning."

(b) *Conditioning the surface by means of "field-current."* "Field-currents" drawn from the surface for the first time, or for the first time after some sort of heat treatment, generally produce a permanent effect upon the surface, a sort of fatiguing effect that makes it more difficult to pull out electrons thereafter. This is shown in Fig. 3 which presents, in the upper curve, the first observations taken on wire II. After pushing the current up to the maximum shown, the currents obtained with diminishing applied potential are all below the corresponding value on the first rising-potential curve. However, the curve then becomes nearly reversibly reproducible until the current is pushed up above its former maximum value, an operation that again lowers the "field-current" for a given gradient. When the emitting surface has once been "conditioned" by drawing from it a large field current, and is not then subjected to further conditioning by current or by heat, it seems to remain fairly constant and the current to become nearly reversibly reproducible (Fig. 3). But intense heat treatment modifies this condition as explained in connection with the data represented in Fig. 4.

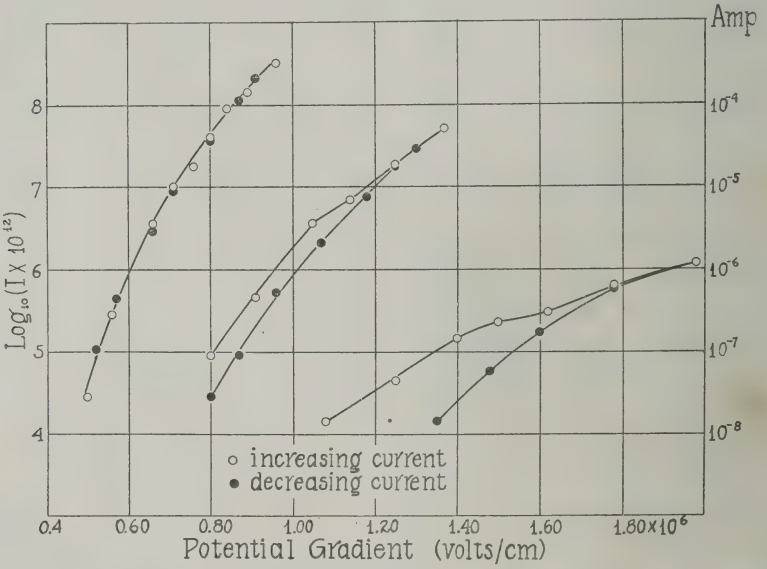

Fig. 4. The curves from left to right represent the data obtained on "current-conditioned" wires which have been heated to 700°K, 1300°K and 2700°K respectively.

Further, field-currents may be drawn for hours at a time without changing appreciably the "critical" potential gradient[9] except in the case of surfaces which have undergone intense heat treatment, and in this case the change due to the heat treatment does not appear to be permanent.

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[9] In what follows, "critical" gradient is the potential gradient needed to produce a "field current" of 9.7 10^{-12} amp.

In one case a gradient of 1.7×10^6 v/cm applied to a surface which had been subjected to extreme heat treatment produced what we shall speak of as a rupture of the surface, for the "field-currents" increased slowly until this gradient was reached and then suddenly jumped up a thousandfold. Two definite spots on the anode opposite the regions of rupture appeared for the first time and these regions gave off nearly the whole of the current, for only two spots could be seen on the outer surrounding cylinder. Not only was the current for a given gradient increased, but the "critical" gradient was changed from 0.74×10^6 to 0.48×10^6 v/cm. This observation was made on wire III. No similar effect was observed on the other wires.

(c) *Conditioning the surface by heat treatment.* The effect produced by heating the wire is so dependent upon the way the impurities on the surface respond to different temperatures, that we shall divide the results of heat treatment into a number of parts, using the temperature range as the criterion of division.

TABLE I

Wire	"Critical" gradient[9] before baking	after baking	Maximum temp. of baking
I	0.48×10^6 v/cm	0.37×10^6 v/cm	360°C
I	0.40	0.38	420°C
II	0.40	0.34	420°C

Long baking of the whole tube at 400°C reduced very slightly the critical potential gradient of a "field-current-conditioned" wire, this in spite of the fact that no change ever took place when the tube stood over night, or for a number of days, provided the vacuum was maintained during this time. The small, but apparently real, change with baking is shown by the data of Table I.

TABLE II

Conditioning "field-current"	"Critical" gradient after "field-current" conditioning (before heating)	(after heating)	Temperature	Total time of heating after conditioning
0.70 m. a.	0.41	0.32	900°K	10 min.
0.24	0.41	0.38	900	15
0.24	0.41	0.41	900	10
0.24	0.41	0.24	1100	5
1.05	0.40	0.27	1100	15
		0.24	1100	30
		0.22	1100	45
		0.21	1100	60
		0.22	1100	90

Heating wire II at 900° to 1100°K largely reduced the "critical" gradient of a "current-conditioned" surface. The "critical" gradient was re-established, however, by the "current-conditioning" process; in fact the phenomenon is roughly reversible, but becomes less pronounced with continued treatment as may be seen from a consideration of the data of Table II.

The effect of raising the tungsten wire to a very high temperature is to increase markedly the critical gradient. This is shown in Table III. It checks a result previously found by Millikan and Shackelford (l. c.). This increase in critical gradient with intense heat treatment is not permanent but disappears on long standing as though the surface underwent slow chemical change.

TABLE III

Temperature	Total time of heating at the particular temp.	Resulting "critical" gradient
1100°K	10 min.	0.39×10^6v/cm
1300	10	0.39
1500	10	0.31
	25	0.26
	40	0.29
1700[10]	20	0.27
1900	10	0.57
	25	0.46
	40	0.34[11]
	55	0.61
1800	15	0.46
	30	0.42
	45	0.68
2300	10	0.74

(d) *Slope of "field-current"-gradient curve a function of "critical" gradient.* The rate of increase of the "field-current" with the potential gradient is large when the "critical" potential gradient is small and vice versa. This is clearly shown in Fig. 4. It is also an observation which had been made previously by the first of the authors. Further, the higher the "critical" gradient, which corresponds to a higher temperature in the heat treatment, the less the constancy and the less the reversibility of the field-current-gradient curves. This is shown clearly in Fig. 4.

(e) *The "field-currents" in general have their origin in a few minute surface spots.* For small currents, less than 10^{-6} amperes, and for corresponding potentials less than 4000 volts, the tube remains perfectly black as viewed in a darkened room. (Currents lower than these may produce a luminous effect if the potential is sufficiently high.) For larger currents luminous spots begin to appear on the inner surface of the cylinder and fluorescent spots to appear on the glass wall directly out from the top of the cylinder. The spots must be due to streams of electrons shot out from active spots on the surface of the wire.

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[10] This temperature and those below it may be too high by 100° to 200°.

[11] This decrease in critical gradient at 1900°K is probably due to thorium which first comes to the surface at this temperature and on continued heating evaporates from it (see Langmuir, Phys. Rev. *22*, 357 (1923)).

The patches of light on the cylinder are reddish-grey in color and as viewed through a direct-vision prism seem to have a continuous spectrum. However, this point should be tested more carefully in an apparatus designed for this purpose.

As the "field-current" increases the spots become brighter and new spots may appear. Some of the spots are fixed in position and for a given current, constant in luminosity; others are slightly changeable in position, and before a steady current state is reached, rather changeable in intensity, and even when the current appears steady there is some variation in these points.

TABLE IV

Wire	"Critical" gradient	
	300°K	900°K
I	0.415×10^6 v/cm.	0.408×10^6 v/cm.
	0.409	0.410
	0.417	0.408
	0.417	0.410
	0.413	0.410
		0.413
I	0.670	0.672
	0.672	0.670
	0.670	0.655
	0.655	
II	0.730	0.730
	0.741	0.736
	0.741	0.741
	0.741	

Sometimes in the "current-conditioning" process, very brilliant spots spring into existence. This is well illustrated by the action of wire II. An irregularity was noticed in the "field-current" and on looking into the tube a new spot was seen on the cylinder near its center. The spot was changeable in intensity but fixed in position. Its intensity slowly decreased and its luminosity became more steady. Thereafter, the current ceased to fluctuate. Another interesting case is that mentioned under (*b*) in connection with the study of wire III. The wire had been heat-conditioned and was giving off very small "field-currents" considering the magnitude of the potential applied. There were only slight traces of luminosity. The next small increase of potential produced the thousand-fold increase in current and two luminous spots had sprung into existence. They furnished practically all of the "field-current," which was rather unsteady. These spots were fixed in position, but very changeable in intensity. The luminosity slowly decreased with continuous operation and the current settled into a more or less steady state.

(f) *The "critical" gradients and the "field-currents" are completely independent of temperature between 300°K and 1000°K.* Only data for the temperature of 900°K will here be recorded, although the effect of lower temperatures was investigated. Wires I and II were studied for this effect; the different "critical" gradients for the same wire are due to the previous conditioning process. The results are recorded in Tables IV and V.

TABLE V

Wire	Potential difference (volts)	Potential gradient (volts/cm)	"Field current" (amp.)			
			900°K	300°K	900°K	300°K
II	1730	0.39×10^{6}	9.7×10^{-12}	9.7×10^{-12}	9.7×10^{-12}	9.7×10^{-12}
	2500	0.57	9.0×10^{-8}	9.0×10^{-8}	9.0×10^{-8}	9.0×10^{-8}
	3000	0.68	1.9×10^{-6}	1.8×10^{-6}	1.8×10^{-6}	1.8×10^{-6}
	3500	0.80	6.0×10^{-6}	6.0×10^{-6}	5.7×10^{-6}	5.7×10^{-6}
	4000	0.91	4.4×10^{-5}	3.9×10^{-5}	4.2×10^{-5}	4.1×10^{-5}
	4550	1.04	2.4×10^{-4}	2.3×10^{-4}	2.3×10^{-4}	2.3×10^{-4}
	4000	0.91	4.2×10^{-5}	4.2×10^{-5}	4.4×10^{-5}	4.4×10^{-5}
	3500	0.80	7.2×10^{-6}	7.1×10^{-6}	7.2×10^{-6}	7.2×10^{-6}
	3000	0.68	6.9×10^{-7}	6.3×10^{-7}	7.2×10^{-7}	6.9×10^{-7}
	2500	0.57	3.0×10^{-8}	3.0×10^{-8}	3.0×10^{-8}	3.0×10^{-8}
	1810	0.41	9.7×10^{-12}	9.7×10^{-12}	9.7×10^{-12}	9.7×10^{-12}
I	8450	1.92	9.0×10^{-7}	9.0×10^{-7}		

(g) *The "critical" gradients and "field-currents" with a tungsten wire at 1100°K.* (The wire is of a just-visible-red color.) The extent of the lowering of the "critical" gradient with this temperature depends upon the magnitude of the "critical" gradient at ordinary temperatures, *zero effect being observed for very low gradients and a considerable effect for higher gradients* (Table VI). The magnitudes of the "critical" gradients at ordinary temperature are, of course, the result of past treatment of the surface. Further, when the gradient is sufficiently high so that the field-currents at 1100°K are observably higher than those at 300°K, *the percentage of increase in current due to this 800° rise in temperature is quite as high for large currents (10^{-4} amperes) as for currents of one thousandth, or even one ten thousandth of this value, thus showing definitely that field currents and thermionic currents are not entirely independent phenomena,* (See §IV(f), below) *since otherwise their effects would be additive.* (See Table VII for the experimental data.)

IV. INTERPRETATION OF THE FOREGOING RESULTS

(a) *Field currents due to "conduction" electrons.* The magnitude and the reversibility of the foregoing field-currents indicate that the electrons which are pulled out of a metal by a sufficiently intense field are the free or conduction electrons[12] of the metal, as Schottky[7] has pre-

TABLE VI

Wire	"Critical" gradient 300°K (volts/cm)	1100°K (volts/cm)
II	0.212×10^6	0.212×10^6
	0.212	0.212
	0.214	0.213
	0.216	0.214
	0.215	
	0.317	0.310
	0.317	0.310
	0.315	
	0.450	0.358
	0.456	0.360
	0.458	0.364
	0.800	0.560
	0.800	0.561
	0.792	0.560
I	0.402	0.315
	0.402	0.319
	0.399	0.322
	0.400	0.335
	0.399	0.335
	0.399	

TABLE VII

Wire	Potential difference (volts)	Potential gradient (volts/cm)	"Field-current" (amp) 300°K	1100°K	300°K
I	2600	0.59×10^6	1.2×10^{-8}	1.5×10^{-8}	1.5×10^{-8}
	3050	0.70	1.2×10^{-7}	1.4×10^{-7}	1.2×10^{-7}
	3500	0.80	6.0×10^{-7}	7.5×10^{-7}	6.0×10^{-7}
	4000	0.91	4.5×10^{-6}	5.4×10^{-6}	4.4×10^{-6}
	4400	1.00	2.1×10^{-5}	2.4×10^{-5}	2.1×10^{-5}
	4750	1.08	5.4×10^{-5}	5.9×10^{-5}	5.4×10^{-5}
	5000	1.14	1.0×10^{-4}	1.1×10^{-4}	1.0×10^{-4}
	4800	1.09	6.3×10^{-5}	6.9×10^{-5}	6.0×10^{-5}
	4200	0.96	1.2×10^{-5}	1.5×10^{-5}	1.2×10^{-5}
	3750	0.85	2.1×10^{-6}	2.7×10^{-6}	2.1×10^{-6}
	3200	0.73	2.4×10^{-7}	3.6×10^{-7}	2.4×10^{-7}
	3000	0.68	9.0×10^{-8}	1.5×10^{-7}	1.0×10^{-7}

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[12] Conduction electrons are here defined as those that are responsible for the Ohm's law effects. They are free merely in the sense that there is no assignable lower limit to the e.m.f. that is required to set them streaming through the conductor.

viously assumed. For first, such large and constant electronic flows, of indefinite duration, would exhaust any other conceivable supply; second, the forces that are here involved are of an altogether different order of magnitude from those necessary to detach any bound electrons of which we have any knowledge. Thus the radiating potential of an atom which holds its outer electrons as loosely as does even sodium, for example, is about 2 volts, and by the application of these 2 volts, the electron is lifted through a distance of about 2×10^{-8} cm, i.e. from the normal position to its first excited position in which the diameter of the atom is about three times its normal diameter.[13] The lower limit to the field-strength, then, which would be required to pull off the electron of sodium from its normal position should be about $2/2\times10^{-8}=100{,}000{,}000$ volts per cm. But these experiments show that field-currents begin to be obtained with the application of a field-strength (potential gradient) of less than 1/200 of this, or 500,000 volts per cm. No bound electron, then, of which we have any knowledge, i.e. no electrons which may be regarded as belonging to particular atoms, are held so loosely as to make it at all possible to consider them as the electrons which here escape. *We therefore regard our fields as reaching sufficiently into the metal to get hold of and pull out some of its conduction electrons.*

(b) *Effect of sub-microscopic irregularities.* The field-currents here studied consist of electrons which escape only from isolated points on the surface where the work function b has been enormously reduced by microscopic geometrical roughnesses, or chemical impurities, or both. The spotted character of the glow on the anticathode is sufficient proof that the discharge actually does come only from specially favored points on the cathode. Further, Schottky[7] has pointed out that it would require a field-strength of the order of 100,000,000 volts per cm merely to counteract (at a distance of 10^{-8} cm, where the electron may be assumed to start) the image-force due to an electron escaping *from a plane surface*; so that neither free nor bound electrons could possibly be pulled away from such a plane surface by the fields used in the foregoing experiments. We can, however, call upon geometrical roughnesses in the surface, of large dimensions in relation to molecular diameters, to reduce the required forces to the observed values. Chemical impurities may obviously assist somewhat in developing such weak points in the surface.

(c) *Conditioning effects of currents, presumably due to positive-ion bombardment.* The conditioning of the surface by means of strong field currents is presumably due to the battering down or rounding off by positive-ion bombardment of the microscopic mountain peaks which act as the electron-emitting points of the surface.

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[13] H. A. Stuart, Zeits. f. Physik **32,** 262 (1925).

The most sensitive means that we have of measuring extremely high vacua is the ionization manometer or Buckley gauge.[14] With this gauge electron currents of the order of milliamperes, such as are here obtained, produce enough positive ions to be easily measurable in the highest vacua that have ever been produced. The electron currents obtained in the present experiments come from a very few points and hence constitute extraordinarily dense electron streams, or pencils, following the direction of the lines of force at the surface. The positive ions formed in these pencils must in these very intense fields return along the same lines of force and bombard almost exclusively the points in the surface at which the electron pencils originate. This theory accounts very satisfactorily for the observed dimming of an anticathode spot with time, the sub-microscopic protuberance having been gradually beaten down into insensitiveness by this bombardment.

(d) *Conditioning effect of heat treatment due to geometrical and chemical changes in the surface.* The lowering of the critical gradient by general heat treatment (Tables I and II) is presumably due to the contamination of the surfaces by emitted gases, while the large increase in the critical gradient by the intense heat treatment of the emitting wire (Table III) is due to the rounding off of surface irregularities supplemented by the removal of surface impurities.

The rounding off of protuberances either by heat or by bombardment should produce all the effects shown in Fig. 4, namely, (1) increase of critical gradient with treatment since both kinds of treatment should reduce the protuberances; (2) decrease of rate of rise of field-currents with applied potential, since the contrast between the peak and its surroundings has been reduced by the treatment and the surface concentration of the field and also of the positive ion bombardment at the sensitive point has become less pronounced; (3) decrease of reversibility with increasing critical gradient, since heavy bombardment from a strong gradient ought to modify a surface more than would gentle bombardment from a weaker one. Indeed, with increasing critical gradient, i.e. increasing energy of bombardment, there is evidence that a definite rupture point of the surface is more and more nearly approached. When it is reached a disruptive discharge occurs by which the cathode may become pitted. This has been shown by point-to-plane discharges.

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[14] O. E. Buckley, Nat. Acad. Sci., Proc. **2,** 683 (1916).

(e) *New proof that the energy of conduction electrons is independent of temperature.* The only preceding theoretical treatment[7] of field-currents assumes them to be composed of thermions escaping under their own energy of agitation through a boundary weakened by the external field. This conception is, we think, altogether irreconcilable with the foregoing data. Indeed, the entire independence upon temperature[15] of the field currents over a range of 700°C constitutes new and striking evidence that "equipartition" does not hold at all for the bulk of the conduction electrons in tungsten at ordinary temperatures. For when these conduction electrons escape as thermions, the law governing their escape is

$$i=AT^n\epsilon^{-b/T} \tag{1}$$

in which b is the work function of Richardson. The correctness of this thermionic equation is attested by a vast amount of experimental work. Now the effect of an externally applied field of such direction as to pull out electrons should be simply to weaken the effective value of the work function b and leave i in the foregoing equation varying as rapidly with T as it always does in thermionic experiments. *The fact, then, that in the present experiments i is not at all dependent upon T over a 700° interval means that the electrons pulled out by the fields here used are not thermions at all.* They might become such at high enough temperatures, but at temperatures up to 1000°K the electrons here pulled out can have no assistance at all from temperature in getting out, i.e., *they do not share in the thermal energy of agitation of the atoms.*

A little, but somewhat uncertain, evidence for this conclusion has been previously obtained by Davisson and Germer,[16] who could bring their two independent methods of measuring b into agreement within one per cent if the electrons within the metal had zero energy, while a discrepancy of 2.7 per cent appeared if the conduction electrons had the energy $3kT/2$. The evidence derived from the specific heats of metals is inconclusive, because the number of conduction electrons within a metal is entirely unknown. The present evidence, on the other hand, appears to be direct, accurate, and unambiguous for the non-participation of the great bulk of "field-current electrons" (conduction electrons) in thermal motion. There must of course be sufficient participation by a few conduction electrons to account for the Peltier and thermo-electric effects, but this is quite consistant with the quantum theory considerations here employed.

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[15] Lilienfeld (l.c.) also reports such independence.

[16] Davisson and Germer, Phys. Rev. **20**, 300 (1922).

The energy of agitation of electrons within tungsten at ordinary temperatures must be altogether analogous to that of the atoms of solid elements at temperatures far below that at which Dulong and Pettits' law holds. The occasional atoms which escape from such a solid follow the Maxwell distribution law[17] and are in thermal equilibrium with the outside vapor, which obeys in all respects the gas laws, but the great mass of the atoms within the solid are devoid of energy of agitation and would be so found if a Maxwell demon could reach in and examine them as the field in the foregoing experiments reaches in and examines the state of agitation of the conduction electrons of the tungsten. *From the point of view here taken the conduction electrons are simply the lightest of the elements which, at ordinary temperatures, have taken on practically no kinetic energy, i.e , have zero specific heat, and which reach equipartition only at very high temperatures. Those of the conduction electrons which at any temperature have escaped from this zero-energy condition are the thermions.* If they carry the total atomic heat of the electrons and if this atomic heat follows the usual quantum law, then their number should increase, at low temperatures, with T^3. This would be consistent with Eq. (1).

(f) *Relations of field-currents and thermionic currents.* We have just seen that *at low temperatures* field currents bear no relation to thermionic currents and that their observed properties lead to the conclusion that the conduction electrons constituting them possess no agitational (temperature) energies at all. But as shown in Table VII, at 1100°K thermionic currents of measurable magnitude (10^{-12} amp.) begin to appear from tungsten and consequently the thermionic equation begins to show evidences of having a role to play in the character of the emission. Thus with increasing potential gradient, the value of the effective work function b is continually reduced and hence the value of the thermionic part of the current (the increase at 1100° over that at 300°) continually rises as is beautifully shown in Table VII so that it makes as large a percentage of the total current when the latter is 10^{-4} amperes (potential difference 5000 volts) as when it is 10^{-8} amperes (potential difference 2600 volts).

Quite similarly, as shown in Table VI, strong fields begin at this temperature to bring into evidence the thermionic part of the current when weak fields are unable to do so. In other words, when the temperature is reached at which the number of thermions escaping without external field is at all comparable with the number constituting the field current at what we have called the critical potential gradient, the decrease in b due to increasing field pushes up the number of emitted thermions (the electrons coming out in accordance with Eq. (1)) slightly faster than the increase in field pulls out field-electrons. Another way of saying this is that field currents are a less rapidly rising function of the field than are thermionic currents (those following Eq. (1) with b regarded as a function of the applied field F.)

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[17] See Germer's recent proof that the Maxwell distribution law holds accurately for thermions escaping into a high vacuum, Phys. Rev. **25**, 795 (1925).

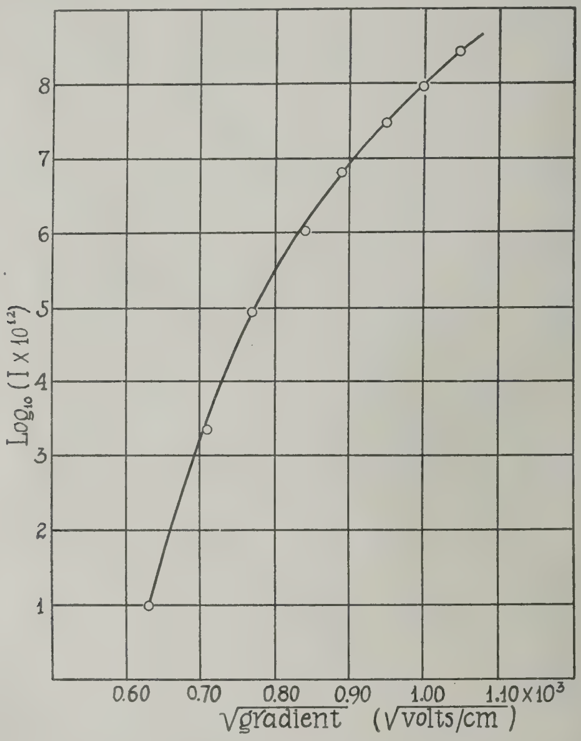

Fig. 5. Variation of the logarithm of the field current with the square root of the potential gradient.

A check on this conclusion may be obtained as follows: If the field currents were made up wholly of electrons, following Eq. (1) we could compute the relation between i and F if we knew how the effective work function b is diminished with increasing F. For sufficiently small values of F, where it is just beginning to influence b appreciably, it is possible to compute what sort of function of F the effective value of the work function is. For at a sufficient distance x_1 from the surface of the wire (a distance large compared to the surface irregularities) it is the image-force alone which must be overcome to cause the electron to leave the surface. The value of this image force per unit charge is $e/4x_1^2$. Every electron must escape which reaches the distance x_1 at which $e/4x_1^2 = F$, i.e., at which $x_1 = \sqrt{e/4F}$. Now the total work necessary to bring an electron out to x_1 is the work b_0 necessary to bring it up to the point x_0 at which the image law begins to be valid plus the integral $\int_{x_0}^{x_1} (e/4x^2 - F)edx$. That is, the work function is

$$b_0 + \int_{x_0}^{\sqrt{e/4F}} (e/4x^2 - F)edx = b_0 + e^2/4x_0 - \sqrt{e^3F} + eFx_0$$

Since x_0 is very small (10^{-8} cm) the last term may be dropped while the first term is the total work necessary to bring the electron out *when there is no field.* Hence $b - \sqrt{e^3F}$ is the work function in the presence of an external field F and the thermionic equation becomes $i = AT^n \epsilon^{-(b-\sqrt{e^3F})/T}$. This equation shows that when T is constant and F alone varies $\log i \propto \sqrt{F}$. This equation should hold so long as all the escaping electrons are brought up to the point x_1 *by their own energy of agitation.* In other words, it should govern the increase in ordinary thermionic emission due to a relatively weak field F. Schottky[18] states that he has tested it for this case and found that the plotting of *log i* against $\sqrt{F}$ yields a straight line.

When, however, we plot for our cold wires log i against $\sqrt{F}$ *using the data given in Figs. 2, 3, or 4 we do not obtain a straight line but instead a curve continually concave toward the* $\sqrt{F}$ *axis* (see Fig. 5). *This means that our field currents do not rise as rapidly with increasing F as is demanded by the thermionic equation.* This is precisely the conclusion we drew from the data in Table VI.

All of our observed phenomena have now been rendered intelligible with the aid of the conceptions which we have herein used.

Norman Bridge Laboratory of Physics,
California Institute of Technology,
October 25, 1925.

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[18] Schottky, Jahrb. d. Radioakt. **12,** 203 (1915).

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THE FIVE ALKALI METALS UNDER HIGH PRESSURE

By P. W. Bridgman

Abstract

Effect of high pressure on the melting constants, electrical resistance and volume of the alkali metals.—(1) *New data for Rb and Cs*, presented in detail elsewhere, are given in three tables. Then, since similar data have previously been obtained for Li, Na and K, the results of a comparative study of all five alkali metals under pressure are given and discussed. (2) *Melting constants.* The general character of the melting phenomena is the same for the alkali metals as for other substances; the melting curve continues to rise indefinitely with increasing pressure, with neither maximum nor critical point. Above 10000 kg/cm^2 there is a reversal of the normal melting points of Na and K, and a moderate graphical extrapolation indicates other reversals also, so that at high pressures we may expect a complete reversal of the order of normal melting temperatures, Cs being the highest and Li the lowest. The fractional change of volume on melting is the same within 25 percent for Na, K, Rb, and Cs, as is also the latent heat of melting per gm atom; for Li the values are only about one-fourth as large. (3) *Electric resistance.* K shows the greatest relative decrease of resistance with pressure above 1400 kg/cm^2; Rb occupies electrically an intermediate position between K and Cs. The effect of pressure on the resistance of Cs is unique in that there is a minimum (at 4000 kg/cm^2). This minimum seems to have no connection with the crystal structure of the solid, but will probably be shown by the liquid also at higher pressures. At low pressures Cs has the maximum negative pressure coefficient of resistance and at high pressures the maximum positive coefficient of all pure metals measured. At high pressures the curve of pressure coefficient of resistance of Cs against pressure has a point of inflection which could not be predicted from the behavior at lower pressures; if other metals behave similarly above the present experimental range, it is possible that the resistance of all metals will eventually pass through a minimum. Such a change for Rb may be expected below 20000 kg/cm^2. This reversal of resistance may be an indication of the first beginning of a quantum break-down, suggested more strongly by the volume relations. The discontinuity of resistance at melting is approximately constant for all the alkalies. (4) *Volume.* Cs is the most compressible solid element yet measured directly. Instead of the atom the electron seems to be the significant unit of structure for volume since the volume per electron and the compressibility per electron do not vary greatly throughout the alkali series, whereas atomic volume and atomic compressibility vary greatly. At atmospheric pressure the electronic volume of K is abnormal, standing between that of Li and Na, but at high pressures there is a reversal. At high pressures the electronic compressibilities of all the alkalies are roughly equal (2.2 to 3.5×10^{-29} at 12000 kg/cm^2), except for K, which is twice as compressible per electron (5.9×10^{-29}). The initial high relative compressibilities of Cs and Rb decrease rapidly with pressure, crossing that for K below 8000 kg/cm^2, while the high compressibility of K persists over a wide pressure range with comparatively small drop. All the evidence indicates an abnormally open electronic structure for K. (5) *Comparison with compressibility of electron gas.* Numerically the compressibility of all the alkalies is of the order of magnitude of that of a perfect gas under a high internal pressure, taking the electron as the gas unit. For K, the compressibility has passed a turning point within the experimental range, and appears to be ultimately headed for the perfect gas value. This may be the beginning of the quantum break-down, which is complete only at remotely high pressures. On the theoretical side, Schottky's theorem, in conjunction with the extrapolated behavior of compressibility, indicates the same break-down at high pressures.

INTRODUCTION

IN a paper now being published by the American Academy, data are given for several of the properties of rubidium and caesium under high pressure. Similar data have been previously published for Li, Na, and K,[1] so that the materials are now at hand for a systematic study of the effect of pressure on the properties of all the alkali metals. The data include the pressure-volume relations, and the effect of pressure on melting and electrical resistance. It is the purpose of this paper briefly to summarize the new data, and then to make a comparative study of the behavior of the five metals under pressure. Such a study may be expected to be of special significance because the effects of pressure on these metals are unusually large; Cs, for example, is by far the most compressible element solid under usual conditions, and is even more compressible over a wide range of pressure than the most compressible organic liquids, such as ether. From a study of these metals, if at all, we may expect light on the question of the ultimate behavior as pressure is increased indefinitely. Recent astronomical speculations deal with densities of 50000; such densities can exist only when the quantum structure of the atoms has entirely broken down and matter is resolved into a gas of electrons and nuclei. Some such break-down of the quantum orbits must of course take place at ordinary temperatures if the pressure is high enough; one of the questions that we shall consider here is whether the high pressure behavior of these metals suggests at all the beginning of such an atomic disintegration.

THE NEW DATA

Melting. The melting data for Rb and Cs are summarized in Table I. In broad features the behavior is the same as that found for all other substances under pressure; the curve of melting temperature against pressure is concave toward the pressure axis, the curve of the change in volume on melting, ΔV, against pressure is convex toward the pressure axis, and the latent heat is comparatively constant. The increase of the latent heat of Cs under pressure is rather greater than usual. These new data on the most compressible metals give no reason to alter the conclusion previously drawn as to the character of the melting curve, namely that the melting curve probably rises indefinitely with continually decreasing curvature, but with neither maximum nor critical point.

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[1] P. W. Bridgman, Phys. Rev. **3**, 154-157 (1914); **6**, 31 and 102 (1915); Amer. Acad. Proc. **56**, 67, 76, and 82 (1921).

TABLE I

Melting data for rubidium and caesium

Pressure (kg/cm^2)		Rubidium			Caesium	
	Temp.	ΔV (cm^3/gm)	Latent heat (kg · m/gm)	Temp.	ΔV (cm^3/gm)	Latent heat (kg · m/gm)
1	38°.7	.0185	2.76	29°.7	.0136	1.65
500	48 .7	163	2.73	41 .4	118	1.68
1000	57 .9	145	2.70	51 .9	105	1.72
1500	66 .5	130	2.66	61 .4	96	1.76
2000	74 .5	119	2.67	70 .2	88	1.80
2500	82 .0	112	2.72	78 .3	83	1.88
3000	89 .1	106	2.76	85 .7	78	1.99
3500	95 .9	101	2.78	92 .4	75	2.14
4000				98 .5	72	2.29

A word should be said about the character of the melting. The melting points found for these metals are materially higher than those usually listed in the literature and the melting was very sharp, both evidence of high purity. It is more than usually difficult to obtain these metals pure; the impurity difficult to remove is not another metal, but oxide, which dissolves in the metal like a foreign metal and depresses the freezing point. Purification demands long slow distillation in high vacuum at the lowest possible temperature. The criterion of sharp freezing is one of the most delicate for high purity, and results should not be accepted for these metals unless the freezing is sharp. Thus the results recently published by Bidwell[2] on the thermo-electric properties of Rb and Cs, which he interprets as due to some sort of internal change in the metals, I believe are much more likely to be due to dissolved impurity. Bidwell's metals left much to be desired as to sharpness of freezing.

Electrical resistance. The data on electrical resistance are too numerous to summarize here, but the most important results, those for the solid metals, are summarized in Table II. It is to be emphasized that the resistance measurements on the solid were made on bare wires; internal stresses introduce too large errors if the metal is enclosed in a glass capillary as has usually been done. In addition to the data of Table II, the detailed paper gives the resistance of the liquid under pressure, the temperature coefficients at atmospheric pressure, a study of the effect of pressure on the temperature coefficient of the solid, and the change with pressure of the discontinuity of resistance on melting.

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[2] C. C. Bidwell, Phys. Rev. **23**, 357-376 (1924).

By far the most important of the new results is the establishment of the minimum resistance of solid Cs. Initially, at atmospheric pressure, the resistance of Cs decreases more rapidly than does that of any other metal, but the rate of decrease rapidly diminishes, until near 4000 kg/cm² there is a flat minimum, and from here on the resistance increases smoothly. This is the only example of a minimum yet found.

TABLE II

Electrical resistance data for Rb and Cs

Pressure (kg/cm²)	Relative resistance of solid bare wire to values for 1 kg/cm², at 0°C		
	Rubidium		Caesium
	0°	35°	0°
1	1.000	1.205	1.000
1000	.845	.982	.863
2000	.733	.840	.779
3000	.648	.740	.729
4000	.583	.663	.709
5000	.531	.602	.713
6000	.490	.553	.728
7000	.456	.514	.756
8000	.428	.481	.794
9000	.406	.455	.833
10000	.387	.434	.879
11000	.372	.418	.931
12000	.360	.406	.994

In a previous paper I made a preliminary announcement that Cs has a second polymorphic modification at high pressures, and that the resistance of this modification increases with pressure. This was an error; the apparent discontinuity which I ascribed to a polymorphic modification turns out to be connected in some way with the separation of impurity and disappears entirely when the purity is sufficiently increased, so that we are left with the perfectly smooth passage of the resistance through a minimum.

The discontinuity of resistance between solid and liquid is approximately constant along the melting curve, decreasing slightly with rising pressure for Rb, and increasing slightly for Cs. The same approximate constancy of the ratio of resistance of solid to liquid has been found for other metals. The temperature coefficient of resistance of solid Rb decreases from 0.00481 at 1 kg/cm² to 0.00365 at 11000, but for solid Cs the temperature coefficient decreases from 0.00496 at 1 kg/cm² to 0.00366 at 6000, and then increases again to 0.00418 at 12000. This is the first example found of a temperature coefficient increasing with rising pressure; it is doubtless connected in some way with the minimum of resistance.

With the improved technique now available, results found previously for K were re-examined. Measurements on the temperature coefficient of K in glass had previously shown a very marked decrease beyond 6000 kg/cm^2,[3] a decrease shown by no other metal. The measurements were now repeated with bare wire, with the results that very little decrease was found beyond 6000, a result agreeing with that for all other metals. Doubtless the former results were due to the constraints exerted by the walls of the glass capillary.

Pressure-volume relations. The pressure-volume relations are summarized in Table III. The pressure range is here 15000 kg/cm^2 against the 12000 of my other work. The greater range was probably responsible for a somewhat lower accuracy, particularly at the upper end of the range. In the detailed paper will also be found a few values for the volume of the liquid phase and also rough measurements of the thermal expansion. The data show that Cs is the most compressible of the solid elements directly measured (indirect inference, however, shows that at least solid hydrogen and helium are much more compressible,[4] but direct observations on these will not be feasible for a long time). At 12000 kg/cm^2 the volume of Cs has been reduced by very nearly the same amount as that of ether, but there is an essential difference in that the

TABLE III

Relative volumes for Rb and Cs

(Referred to values for 1 kg/cm^2)

Pressure (kg/cm^2)	Rubidium 50°C	Caesium 50°C
1	1.000	1.000
1000	.953	.941
2000	.914	.898
3000	.883	.866
4000	.857	.839
5000	.836	.816
6000	.819	.796
7000	.803	.777
8000	.789	.760
9000	.777	.745
10000	.766	.731
11000	.756	.718
12000	.746	.706
13000	.737	.694
14000	.729	.683
15000	.721	.672

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[3] P. W. Bridgman, Amer. Acad. Proc. **56**, 140 (1921).

[4] P. W. Bridgman, Amer. Acad. Proc. **59**, 198 (1924).

compressibility of Cs is less affected by pressure than is that of ether. The initial compressibility of Cs is less than that of ether and its compressibility at 12000 greater, so that at higher pressures (20000 kg/cm², for example) the volume of Cs will be very materially less than that of ether.

Comparative Discussion

Melting data. In Fig. 1 are plotted in one diagram the melting points of the five alkali metals as a function of pressure. The most interesting feature is the crossing of the curves for Na and K, so that above 10000 kg/cm² the melting point of K is higher than that of Na, reversing the normal order. The diagram suggests strongly that there are other crossings at higher pressures; it seems almost certain that K will cross Li, and highly probable that Na will also cross Li. It is more difficult to estimate the future course of the curves for Rb and Cs, because these are given over only a small range, but it is not at all improbable that

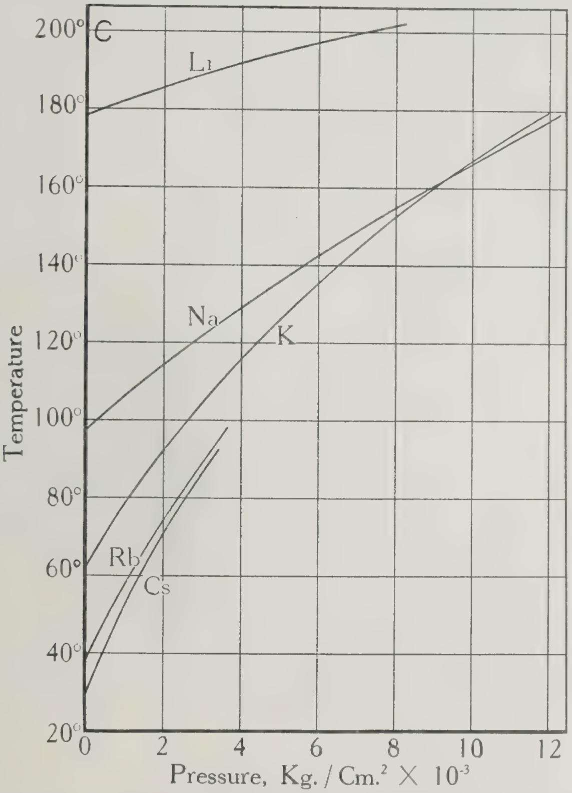

Fig. 1. The melting temperatures of the alkali metals as a function of pressure.

these two curves will eventually cross all the others, so that at sufficiently high pressures the order of melting may be Cs, Rb, K, Na, and Li, the reverse of the usual order. This is not at all an unnatural state of affairs. At high pressures we may expect the atoms to become so packed in together that they find difficulty in melting; this packing effect will increase with the complexity of the atom, and the most complicated atom, Cs, will have the highest melting point.

The pressure at which this reversal of the ordinary melting points will be accomplished may be estimated by graphical extrapolation to be of the order of 25000 kg/cm^2. Such a pressure is comparatively low, much too low to produce those ultimate effects to be expected at extreme pressures when the quantum orbits break up. Under such pressures it will be shown that the volume relations of K differ from those of the other metals; it might be thought that the crossing of the melting curves is similarly an effect due to the unique behavior of K. This, however, I do not believe to be the case; the shape of the melting curves themselves, and also the fact that if melting temperature at atmospheric pressure is plotted against atomic number, K will be found to lie smoothly with the other metals, both suggest that K is not unusual with regard to melting. The peculiar volume relations of K to be discussed later do not seem strongly to affect the melting behavior.

The other melting data relating to change of volume and latent heat are also significant. It is evident that melting is an atomic phenomenon, and the five alkali metals should be compared on an atom for atom basis. Table IV shows the latent heat of melting at atmospheric pressure per gm atom. On passing from the solid to the liquid state approximately the same heat is absorbed per atom by all the alkalies (except Li). Under high pressure the latent heats vary in a complicated way, but not by large amounts, so that over the entire pressure range the generalization holds that the latent heat of melting per atom is approximately the same.

TABLE IV

Melting data at atmospheric pressure

Metal	Latent heat (kg · m/gm · atom)	Fractional change of volume
Li	49	.0060
K	215	.0231
Cs	219	.0256
Rb	236	.0284
Na	271	.0271

Table IV shows also that, except for Li, the fractional change of volume on melting is approximately the same, that is, on passing from the solid to the liquid state an atom of an alkali metal experiences a definite fractional increase of volume.

Lithium is unique in its melting phenomena. The reason doubtless is to be sought in the structure of the atom; the number of electrons is so small, only three, that the external symmetry of the atom must be much lower than that of the other four alkalies.

Electrical resistance. Unlike many of the other properties, the electrical resistance of the alkali metals does not vary smoothly in the same direction throughout the series. Thus the specific resistance at 0°C at atmospheric pressure decreases from Li to Na, and then increases again from K to Rb to Cs. The numerical values of the specific resistance are respectively 8.6×10^{-6}, 4.3, 6.1, 11.6, and 19. A somewhat more satisfactory basis for comparison is the "conductivity per atom," which is obtained by dividing the specific conductivity at a temperature one half the characteristic temperature by $N^{1/3}$, where N is the number of atoms per cc. This is discussed more in detail in my forthcoming Solvay Conference report. If "conductivity per atom" is plotted against atomic number, a comparatively smooth curve will be found with a very pronounced maximum between K and Rb. A similar reversal within the series is shown by the pressure effects. In Fig. 2 the relative resistance at 0° is plotted against pressure. It is evident that there is some sort of a turning point between K and Rb.

The resistance of most metals decreases with rising pressure, but there are seven metals whose resistance increases. Among some 50 metals studied, the series of the alkali metals includes the numerical extremes of maximum positive and maximum negative pressure coefficients of resistance.

It is of interest that the abnormal pressure effects of both Li and Cs do not seem to be associated with the crystal structure of the solid but are more intimately connected with the atoms themselves. This is shown by the fact that the resistance of Li increases under pressure in the liquid as well as in the solid state. A corresponding experiment could not be made on the resistance of liquid Cs because within the temperature range of these experiments the liquid freezes at a pressure below that of the minimum resistance. But at 97° the freezing pressure is very close to that of the minimum resistance. The resistance of solid and liquid at this temperature was plotted in one diagram as a function of pressure, multiplying the resistance of the solid by such a factor as to remove the discontinuity at the freezing point. In this way a curve was obtained passing perfectly smoothly through the melting point. The obvious inference is that the crystal structure of the solid has nothing to do with the minimum, and that at higher temperatures the resistance of the liquid as well will show a minimum.

A question of great importance for theories of resistance is whether the minimum resistance shown by Cs, the most compressible of the metals, will be shown by the other metals also at pressures high enough. This question can be answered only by some sort of extrapolation. Such an extrapolation is not easy from the curves of resistance given in Fig. 2. If, however, we plot $(1/w)(\partial w/\partial p)_\tau$ as a function of pressure, where w is resistance, we get something more suggestive as to the behavior at high pressure. For Cs, this quantity starts negative and crosses the axis at the pressure of the minimum, which is about 4400 kg/cm². The curvature against pressure is convex upward at pressures below 8000 kg/cm², but here there is a point of inflection, and above 8000, $(1/w)(\partial w/\partial p)_\tau$ increases at an accelerated rate with increasing

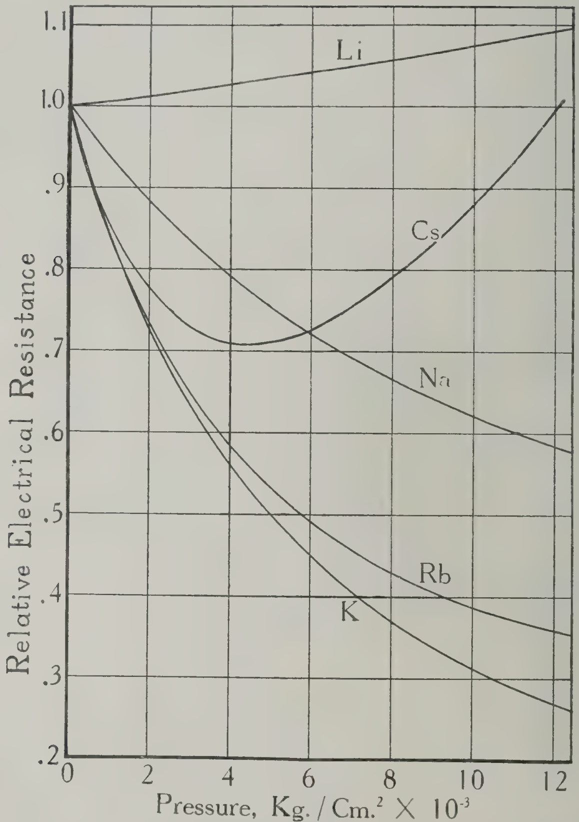

Fig. 2. The relative electrical resistances at 0°C of the alkali metals as a function of pressure.

pressure. If this inflection is characteristic of the behavior of other metals at still higher pressures, then the resistance of each of them must also ultimately pass through a minimum. The shape of the curve for Rb indicates that this may well occur at some pressure below 20000 kg/cm^2.

We next have to ask what is the theoretical significance of this minimum resistance. The theory of electrical resistance which I have developed[5] represents the conduction electrons as passing through the substance of the atoms and encountering resistance where they make the jump from atom to atom. A minimum resistance is to be thought of as due to the fact that as the pressure is increased a point is reached beyond which the electrons find it increasingly difficult either to make the jump from one atom to the next or to get through the atom. Such interference with the electron is not surprising in a complicated structure distorted at high pressure. The minimum resistance is perhaps in Cs to be regarded as the first shadowing forth of the ultimate disintegration of the quantum orbits under extreme pressure. It is significant that the effect is first found in the most compressible metal with a complicated atomic structure.

Volume relations. In discussing melting phenomena we have seen that the atom is the significant unit of structure, as is shown for example by the fact that the latent heat of melting per atom is nearly the same for the four heavy alkalies. This is as we would expect, since the atoms pass as a unit from the liquid to the solid phase. But now that we are to discuss volume relations, it will appear that the electron, the ultimate constituent of the atom, is the more significant unit of structure; this is suggested by the fact that the contributions made to the volume or to the compressibility per electron vary much less from one alkali to another than do the contributions per atom.

We first compare the volume per electron in the five metals as a function of pressure. The volume per electron is obtained from the volume per atom by dividing by the atomic number plus 1 (that is, we are obtaining the average volume occupied by one discrete piece of electricity, whether positive or negative, the nucleus counting as one). The volume per atom is the atomic weight multiplied by 1.66×10^{-24} (the weight of the atom of hydrogen) divided by the density. Thus we find, for example, the volume per electron of Li at atmospheric pressure is $6.94 \times 1.66 \times 10^{-24}/4 \times .53 = 5.43 \times 10^{-24}$ cm^3.

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[5] P. W. Bridgman, Phys. Rev. **19**, 269-289 (1917); **17**, 161-194 (1921); **19**, 114-134 (1922); Report of the Solvay Conference, Brussels, 1924 (not yet published).

In Fig. 3 is plotted the volume per electron as a function of pressure. Li has the largest and Cs the smallest electronic volume, that is, the quantum orbits are closely packed in Cs but loosely packed in Li. The electronic volume of Li at atmospheric pressure is 2.6 fold greater than that of Cs. On the other hand, if we compared atomic volumes, we would find the volume of Li to be least, and that of Cs greatest, 5.3 times that of Li. The variability of volume throughout the series of the alkalies is thus twice as great when expressed in terms of the atom as when expressed in terms of the electron.

At atmospheric pressure the electronic volume of K is greater than that of Na, a reversal of order. At high pressures, however, the curves for K and Na cross. This is the first of several pieces of evidence that the electronic structure of K is abnormally loose.

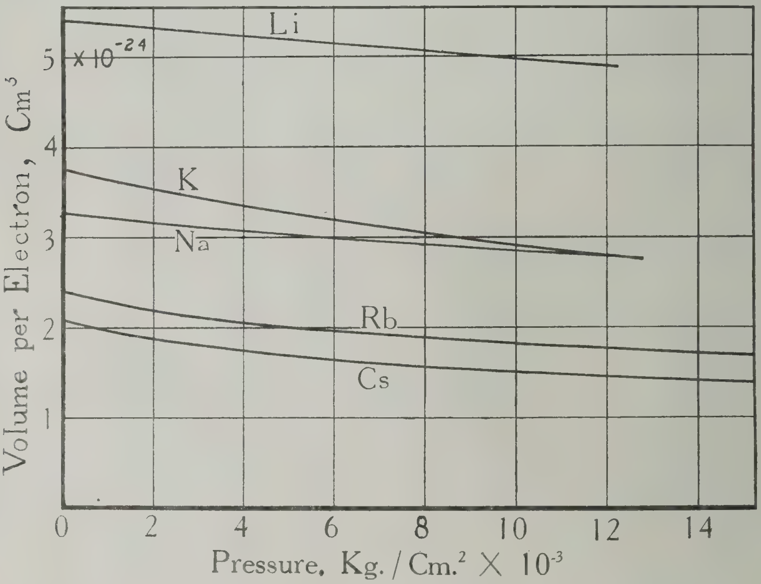

Fig. 3. The volume per electron in cm³ of the alkali metals as a function of pressure.

It is evident from Fig. 3 that the shapes of the curves of electronic volume against pressure are distinctly different for the different alkalies. This difference is brought out much more strikingly in Fig. 4 in which is plotted the instantaneous compressibility, $(1/v)(\partial v/\partial p)_T$, as a function of pressure. If the curves of volume against pressure were of the same shape, the curves of $(1/v)(\partial v/\partial p)_T$ against pressure would be the same for all the metals. This is evidently far from being the case. Not only are the absolute values of $(1/v)(\partial v/\partial p)_T$ quite different, but the shapes of the curves are very different. This has a bearing on speculations of Richards[6] as to the internal pressures of the alkalies. In endeavoring to find some rational basis for extrapolation, he made the assumption that the pressure-volume curve at low pressures of a comparatively incompressible alkali was of the same shape as the pressure-volume curve at high pressure of a more compressible alkali; that is, if all the ordinates of the pressure-volume curve of one metal were multiplied by an appropriate constant and then the curve slid bodily along the pressure axis, the curve so found would coincide with the prolongation into a region as yet unreached experimentally of the pressure-volume curve of another alkali. In particular, he applied this method of extrapolation to Na and K. At the time that he did this, these data for Cs and Rb were not available. These new data show definitely that the assumed connection between the different metals

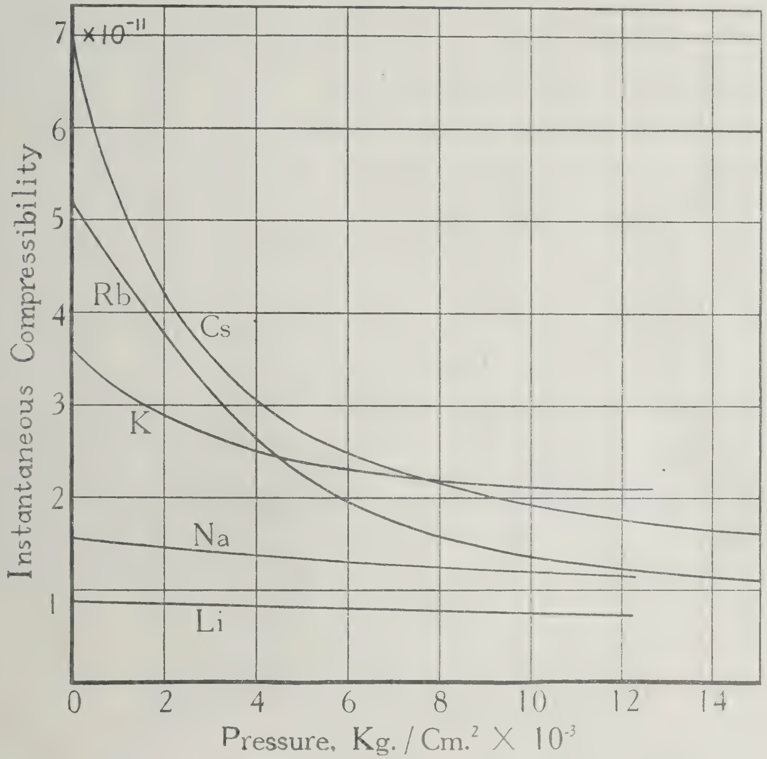

Fig. 4. The instantaneous compressibility $(1/v)(\partial v/\partial p)_T$ in Abs. C.G.S. units, of the alkali metals as a function of pressure.

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[6] T. W. Richards, Jour. Amer. Chem. Soc. **45**, 422-437 (1923).

does not exist, for if it did, the curves could not cross in the way they do. Richard's method of extrapolation can therefore be regarded as only roughly suggesting what to expect at high pressure; it is probable, however, that the approximation was sufficiently good for the purpose for which Richards used it.

The most striking feature of Fig. 4 is the crossing of the curves for Cs and Rb by that of K; this means that K retains its compressibility to an abnormal degree at high pressures. This again points to a looseness of internal structure. Another striking feature is the great progressive change in the character of the curves throughout the series. In 12000 kg/cm^2 the compressibility of Li drops to 0.83 of its initial value, whereas that of Cs drops to 0.23. The rapid drop of compressibility with increasing pressure is partly due, especially for the more compressible metals, to a taking out of "slack" from the structure by pressure. In the most complicated structure, that of Cs, the possibility of taking out slack is most rapidly exhausted, giving the most rapid drop of compressibility with increasing pressure.

The extent to which the "slack" in the structure is responsible for the initial behavior is further indicated by Table V which shows the compressibility per electron, that is, the actual loss in volume per electron under a pressure increase of 1 kg/cm^2, at 1 and 12000 kg/cm^2, for the 5 metals. Under 12000 the approximate constancy of the compressibility per electron for all the metals (except K) is striking, especially when compared with the initial variability. Li has the greatest compressibility per electron at high pressure, as we would expect because of its more open structure. However, the difference is not as great as might be expected. At 12000 the electrons are packed 3.3 times more loosely in Li than in Cs, but the compressibility is only 1.4 times greater. K is an outstanding exception, both in its initial compressibility (too great to lie in a smooth series with the others) and in its persistent compressibility at high pressures, about twice as high as the average of the others.

TABLE V

Volume compression per electron per kg/cm^2

Metal	Electronic compression Atms. pressure	 12000 kg/cm^2
Li	4.7×10^{-29}	3.5×10^{-29}
Na	5.1	3.2
K	13.5	5.9
Rb	12.5	2.2
Cs	14.5	2.5

Finally we have to consider whether there is any indication within the pressure range reached experimentally of the beginning of the breakdown of the quantum structure which we may expect must be inevitable if the pressure can only be pushed high enough. An inquiry of this sort must, of course, be highly speculative. We take as our clue the recent speculations of astronomers that in the interiors of the stars matter may be disintegrated into a gas of electrons and nuclei.

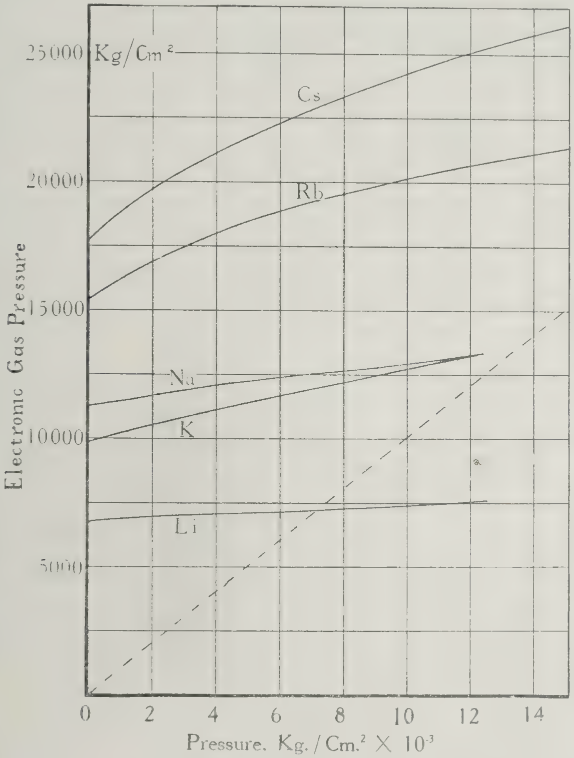

Fig. 5. The electronic gas pressures (that is, the pressures which would be exerted by the electrons and nuclei if they were in the condition of a perfect gas under the actual volume of the metal) of the alkali metals at 0°C as a function of external pressure.

It is in the first place to be noticed that the pressures which would be exerted by these alkali metals if electrons and nuclei constituted a perfect gas are not excessively high. The material for such a calculation is already at hand; we have merely to divide the reciprocal of volume per electron (number of electrons per cm^3) by 2.7×10^{19}, the number of gas molecules per cm^3 at 0°C at 1 atmosphere. In this way the curves of Fig. 5 were obtained. The pressures are of the order of tens of thousands of kilograms per cm^2, which is the order of experimentally obtainable pressures. It is therefore not extravagant to think that experimentally obtainable pressures may at least initiate the reversion to the perfect gas condition. The direction in which the quantum forces act is shown in the figure by the location of the gas pressure curve with respect to the 45° line. The curve for Li crosses this line at 7000; above 7000 the electrons in the perfect gas state would not be able to withstand the external pressure, so that if the quantum forces were removed the structure would collapse. Hence above 7000 the quantum forces distend the structure, whereas below 7000 they prevent it from flying apart. It is also evident from the figure that below 15000 kg the quantum forces in Na and K will change from an expansive to a compressive character. It seems probable that Rb and Cs will similarly change at considerably higher pressures.

When the structure breaks down completely into a perfect gas, the gas pressure curve will coincide with the 45° line, or at least will run parallel to it. The figure shows that any such state of affairs is remote, but there are two indications of the beginning of an approach to it. In the first place, it is evident that K comes nearest of the three lightest alkalies to satisfying this condition, because the slope of its gas pressure curve is closest to 45°. But if there is ever going to be coincidence or parallelism with the 45° line, it is evident that the gas pressure curve must be concave upwards, whereas at low pressures all the curves are concave downward, as is shown in the figure most unmistakably by the entire course of the curves of Rb and Cs. Now this necessary reversal of curvature is indeed shown, well beyond experimental error, both by K and Li, although the effect is not large enough to be well marked in the diagram, and probably is shown by Na also, although it is not so certain that experimental error may not enter here.

The effect is exhibited more clearly if we consider the compressibility instead of the volume. The question is whether the compressibility of the solid alkali metals has features in common with the compressibility of a perfect gas. The compressibility of a perfect gas is $(1/v)(\partial v/\partial p)_\tau = -1/p$. But when we attempt to apply this expression to our solid metals we encounter the difficulty of not knowing the internal pressure. We avoid this difficulty by eliminating p by dividing both sides of the equation by v_e, where v_e is the average volume occupied by one electron, using the gas law $pv_e = 1.35\times 10^{-16}\tau$, and obtain:

$$\frac{1}{v_e}\left[\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_\tau\right] = \frac{-1}{1.35\times 10^{-16}\tau} = -2.4\times 10^{13} \text{ at } 300°\text{K}.$$

The material is at hand for a calculation of $(1/v_e)(1/v)(\partial v/\partial p)_\tau$, which we will call the "gas function," as a function of pressure. The results are shown in Fig. 6. It is significant that the gas function is of the order of magnitude of -2.4×10^{13}, which is the value it would have if the solid were to act like a perfect gas under some unknown but high pressure and in which the *kinetic unit is the individual electron.* If we assumed that the atom were the unit, the gas function would be of a different order of magnitude. The approach of the gas function to the value of a perfect gas is closest for Cs and most remote for Li. In speculating now as to the behavior at very high pressures, the shape of the curve for the gas function is significant. The curves for Cs and Rb are still receding from the perfect gas value at the highest pressures reached experimentally, whereas for K a reversal has been reached at 7000 or 8000 kg/cm^2, and above this pressure the gas function of K has started to approach more closely to the value for a perfect gas. It is tempting to see in this the beginning of the quantum breakdown.

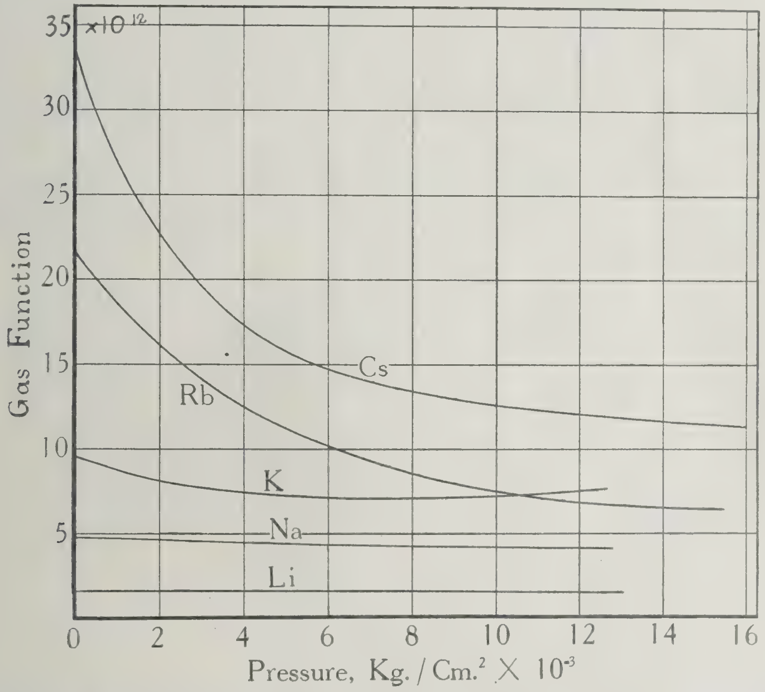

Fig. 6. The "gas function" $(1/v)(1/v)(\partial v/\partial p)_\tau$ of the alkali metals as a function of external pressure. If the metals acted like a perfect gas of electrons and nuclei, the gas function would have the constant value 24×10^{12}.

Apart from this experimental evidence, we may obtain some theoretical light on the question of the ultimate behavior under exceedingly high pressures from a theorem due to Schottky.[7] He finds for any system in which there are forces between the elements given by the ordinary inverse square laws of electromagnetism and in which the elements move under these forces as if they had mechanical mass, whether or not the motion is in addition subjected to quantum forces, the following equations:

$$\left(\frac{\partial \overline{L}}{\partial p}\right)_\tau = 3v + \tau\left(\frac{\partial v}{\partial \tau}\right)_p + 4p\left(\frac{\partial v}{\partial p}\right)$$

$$\left(\frac{\partial \overline{E}}{\partial p}\right)_\tau = -3v - 2\tau\left(\frac{\partial v}{\partial \tau}\right)_p - 5p\left(\frac{\partial v}{\partial p}\right)_\tau ,$$

where $\overline{L}$ is the average internal kinetic energy of motion of the elements, and $\overline{E}$ is the average electromagnetic potential energy. The total internal energy $\overline{U}$ of the system is of course given by $\overline{U}=\overline{E}+\overline{L}$. The equations in the form above were not given by Schottky, but may be deduced from equations given by him by using the ordinary thermodynamic relation

$$\left(\frac{\partial \overline{U}}{\partial p}\right)_\tau = -\tau\left(\frac{\partial v}{\partial \tau}\right)_p - p\left(\frac{\partial v}{\partial p}\right)_\tau .$$

At 0°K we have rigorously

$$\left(\frac{\partial \overline{L}}{\partial p}\right)_\tau = 3v + 4p\left(\frac{\partial v}{\partial p}\right)_\tau$$

$$\left(\frac{\partial \overline{E}}{\partial p}\right)_\tau = -3v - 5p\left(\frac{\partial v}{\partial p}\right)_\tau .$$

These relations are also approximately true at other temperatures, for on substituting numerical values for ordinary solid metals it appears that the term $\tau(\partial v/\partial \tau)_p$ is unimportant. Now in the equations as last given the term v is positive and $p(\partial v/\partial p)_\tau$ is negative. At zero pressure only the term v contributes, and $\overline{L}$ increases with increasing pressure and $\overline{E}$ diminishes. But with increasing pressure v diminishes and $p(\partial v/\partial p)_\tau$ increases. Will the second term eventually become larger than the first? We attempt to answer this by plotting $-(p/v)(\partial v/\partial p)_\tau$ against pressure for the five alkali metals. Fig. 7 shows the result. If $-(p/v)(\partial v/\partial p)_\tau$ becomes equal to 0.6, the direction of variation of $\overline{E}$ changes, and if it reaches 0.75, the direction of variation of $\overline{L}$ changes.

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[7] W. Schottky, Phys. Zeits. **21**, 232 (1920).

Again K is the most suggestive metal. For it, $(p/v)(\partial v/\partial p)_\tau$ is nearly linear against pressure; as a matter of fact at low pressures the curve is slightly concave toward the pressure axis, but at high pressures it becomes slightly convex. $(p/v)(\partial v/\partial p)_\tau$ therefore rises at an accelerated rate as pressure increases, and the critical value 0.6 will be reached at a pressure near 30000 kg. The curves for the other metals are also flattening out at a rapid rate, so that is it probable that for all the alkalies the critical value will be eventually exceeded.

What now is the significance of the change of L and E? Initially the state of affairs is plain. In general an increase of L means an increase of rapidity of motion of the electrons in their orbits, which means an approach on the average to the attracting nuclei. The same approach to the nuclei which increases L brings the electrons into stronger parts of the fields of the nuclei and thus at the same time provides for the decrease of E. This approach to the nuclei may be thought of as signifying a compression of the atoms under pressure, as Schottky suggested, or it may be thought of as follows. As we proceed through the series of the chemical elements from simpler to more complex, it is well recognized that the electron orbits penetrate more and more deeply toward the nucleus, and at the same time become more eccentric. The same sort of thing may very naturally be produced also when we push the electron orbits into closer juxtaposition by increasing pressure, so

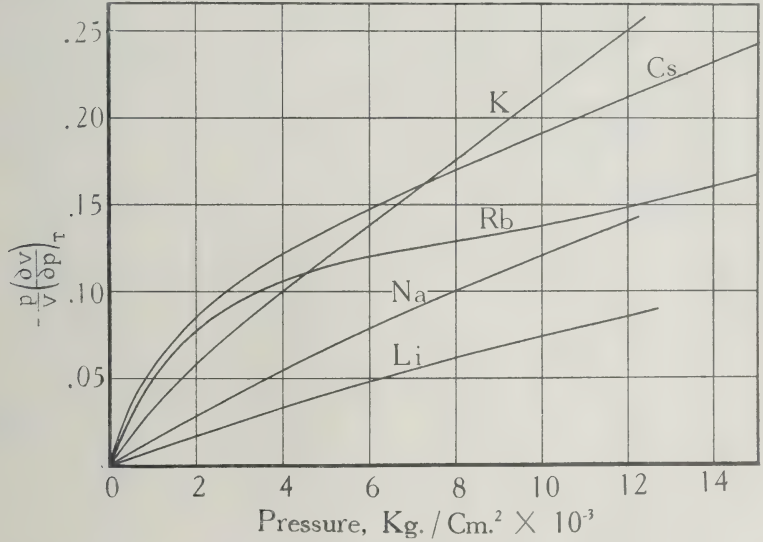

Fig. 7. The function $-(p/v)(\partial v/\partial p)_\tau$ of the alkali metals as a function of external pressure.

that the initial increase of L and decrease of E with increasing pressure is accounted for by a deeper penetration of the orbits toward the nuclei. But now at higher pressures, how are we to account for a decrease of L and an increase of E, if according to our argument this means orbits described at greater distances from the nuclei? The difficulty is overcome if the electron orbits break down, allowing an approach to a more uniform distribution in space of electrons and nuclei. The electrons now do not penetrate so closely to the attracting nuclei, so that on the average L is smaller and at the same time E increases, both in spite of a continued decrease of total volume. But this sort of break-down means an approach to the condition of a gas. It thus appears that the dilemma to which Schottky's theorem, in conjunction with the experimental behavior of the compressibility of the alkali metals, forces us, is resolved by a break-down of the quantum orbits at sufficiently high pressures, and an approach to the condition of a gas.

Jefferson Physical Laboratory,
Harvard University,
October 4, 1925.

PHYSICAL REVIEW JANUARY, 1926 VOL. 27

BATEMAN'S EXTENDED ELECTRODYNAMICS, AND THE MASS AND RADIATION REACTION OF AN ELECTRON

By Meyer Salkover

Abstract

From Bateman's earlier stress-energy tensor, there are deduced by analogy with the momentum and energy equations based on the classical electromagnetic stress-energy tensor, an extra-classical body-force and a condition that may be understood to state the conservation of charge in combination with the Lorentz transformation. It is then shown how this procedure may be reversed so as to derive, from the new body-force and the condition just mentioned, Bateman's tensor with all of its components physically interpreted. Next the mass and radiation reaction of an electron in non-uniformly accelerated, non-periodic motion are calculated from the force (classical and extra-classical) exerted on it by its own field, on the assumptions that the electron is spherical in a rest-system and has a centrally symmetrical distribution of charge. Both come out zero. The result for the radiation reaction is new. Finally the same result for the mass is obtained from the total momentum of the field of an electron in uniform, or quasi-stationary, motion. The present method differs from one recently published by Bateman in not using the restricted relativity transformation for tensors, and in requiring of the distribution of charge only that it be centrally symmetrical.

Introduction

To the stress-energy tensor T^e of classical electrodynamics, comprising the stress-system $X_x^e, X_y^e \ldots Z_z^e$, the energy-flux (Poynting's) vector $\mathbf{S}^e$ and related density of momentum $\mathbf{G}^e$ and the energy-density W^e as deducible from the equations of Maxwell and Lorentz, Bateman has successively added new tensors[1] designed to remedy defects of the classical theory. The fundamental one of these tensors, and the only one that will be considered here, is T^s, having as components

$$X_x^s = -2\psi\frac{\partial^2\psi}{\partial x^2} + \left(\frac{\partial\psi}{\partial x}\right)^2 + \left(\frac{\partial\psi}{\partial y}\right)^2 + \left(\frac{\partial\psi}{\partial z}\right)^2 - \frac{1}{c^2}\left(\frac{\partial\psi}{\partial t}\right)^2$$

$$X_y^s = Y_x^s = -2\psi\frac{\partial^2\psi}{\partial x\partial y}$$

$$W^s = 2\psi\frac{\partial^2\psi}{\partial t^2} + \left(\frac{\partial\psi}{\partial x}\right)^2 + \left(\frac{\partial\psi}{\partial y}\right)^2 + \left(\frac{\partial\psi}{\partial z}\right)^2 - \frac{1}{c^2}\left(\frac{\partial\psi}{\partial t}\right)^2$$

$$S_x^s = c^2G_x^s = -2\psi\frac{\partial^2\psi}{\partial x\partial t}$$

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[1] H. Bateman, Phys. Rev. **20**, 243 (1922); Bull. Nat. Res. Council, **24**, p. 99 (1922); Messenger of Mathematics **52**, 116 (1922); Ibid. **53**, 145 (1924); Phil. Mag. **49**, 1 (1925).

where ψ is a retarded scalar potential defined by

$$\psi = \int \left[\rho\sqrt{1-(v^2/c^2)}\,\right]_{t-r/c}(dV/r)$$

and consequently satisfying the differential equation

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}-\frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2}=-\rho\sqrt{1-(v^2/c^2)}$$

Since the right side of this equation is an invariant with respect to the Lorentz transformation, as is also the differential operator on the left side, it follows that the potential ψ is such an invariant. The tensor T^s is then readily shown to be a symmetrical world-tensor[2] with the same transformational properties as T^e.

The components of the body-force associated with T^s are determined by relations of the type

$$F_x{}^s=\frac{\partial X_x^s}{\partial x}+\frac{\partial X_y^s}{\partial y}+\frac{\partial X_z^s}{\partial z}-\frac{\partial G_x^s}{\partial t} \tag{1}$$

which are identical in form with the relations between the classical body-force

$$\mathbf{F}^e=\rho\left(\mathbf{E}+\frac{1}{c}\mathbf{v}\times\mathbf{H}\right)$$

and the tensor T^e. The results may be combined in the vector equation

$$\mathbf{F}^s=2\psi\nabla\left\{\rho\sqrt{1-(v^2/c^2)}\,\right\}\,. \tag{2}$$

Corresponding to the classical energy-equation, we have also

$$\mathbf{v}\cdot\mathbf{F}^s+\mathrm{div}\mathbf{S}^s+\frac{\partial W^s}{\partial t}=0 \tag{3}$$

provided that

$$\psi\frac{d}{dt}\left\{\rho\sqrt{1-(v^2/c^2)}\,\right\}=0 \tag{4}$$

It is possible to proceed in another manner, following the usual treatment of classical electron theory. If we assume Eq. (2), then by an integration of $\mathbf{F}^s$ over all space and a reduction by means of Green's Theorem, the expressions previously labeled as X_x^s, X_y^s . . . Z_z^s and $\mathbf{G}^s$ are obtained and seen to have physical meanings consistent with the names assigned to them. Details will not be given; the process, though rather lengthy, is direct, and offers no essential difficulties. Eq. (1) follows as a corollary. In the same way, starting with an integration of the activity of the body-force, $\mathbf{F}^s \cdot \mathbf{v}$, we can derive the rest of the tensor T^s and Eq. (3), if

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[2] M. v. Laue, Die Relativitätstheorie, 4. Aufl., 1. Bd., p. 102.

$$\frac{d}{dt}\left\{\rho\sqrt{1-(v^2/c^2)}\right\}=0\ .$$

The last assumption, which is not altogether the same as Eq. (4), may be granted, since it amounts to the conservation of charge as combined with the Lorentz transformation.

Mass and Radiation Reaction

The reaction on an electron of its own field will now be considered. The electron will be taken as spherical when at rest, with a volume charge distributed symmetrically about the center, but otherwise arbitrarily. The motion of the electron will be unspecified except for the supposition that there is always a reference system of the type dealt with in the restricted theory of relativity in which the electron is momentarily at rest, with acceleration and derivative of acceleration not varying from point to point, and that, relative to this system, the electron is spherical and has the stationary distribution of charge.

On these assumptions, the classical reaction, so far as it depends on the acceleration ($\mathbf{f}$) and derivative of the acceleration ($\dot{\mathbf{f}}$), is[3]

$$-(\mathbf{f}/6\pi c^2)\int \rho dV \int \rho' dV'(1/(R^2+R'^2-2RR'\cos\theta)^{1/2})+e^2\dot{\mathbf{f}}/6\pi c^3$$

where ρ and ρ' are the densities of charge at volume elements dV and dV' which lie, respectively, at distances R and R' from the center, along radii vectors enclosing the angle θ.

To get the extra-classical reaction, we start with Eq. (2). Here, to allow for the rest-system used, we put $v=0$. The part of ψ due to element of charge de at a field-point relative to which the position of de is given by the vector $\mathbf{r}$ is

$$de\left[\sqrt{1-(v^2/c^2)}\right]/4\pi\left[r(1+(\mathbf{r}\cdot\mathbf{v}/cr))\right]$$

where the bracketed quantities must be assigned the values pertaining to the previous time $t-[r]/c$. This expression, reduced by means of known series expansions[4] so as to involve only magnitudes evaluated at the time t becomes, as far as terms in $\dot{\mathbf{f}}$,

$$\frac{de}{4\pi}\left(\frac{1}{r}+\frac{1}{2}\,\frac{\mathbf{f}\cdot\mathbf{r}}{rc^2}-\frac{1}{3c^3}\dot{\mathbf{f}}\cdot\mathbf{r}\right)$$

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[3] L. Page, Introduction to Electrodynamics, pp. 51 52.

[4] Ref. 3, pp. 39, 40.

Next, changing de to $\rho' dV'$, multiplying by $2\nabla\rho dV$, and integrating twice through the electron, we have, omitting the electrostatic term that contributes nothing,

$$\frac{\mathbf{f}}{4\pi c^2 f}\int dV \cos\alpha(\mathbf{f}\cdot\nabla\rho)\int\frac{\rho' dV'(R'\cos\theta-R)}{\sqrt{R^2+R'^2-2RR'\cos\theta}}+\frac{e\dot{\mathbf{f}}}{6\pi c^3}\int\cos^2\beta\frac{d\rho}{dR}dV$$
$$-\frac{\mathbf{f}}{4\pi c^2}\int\rho_{R=a}\cos^2\alpha dS\int\left[\frac{\rho' dV'(R'\cos\theta-R)}{\sqrt{R^2+R'^2-2RR'\cos\theta}}\right]_{R=a}$$
$$-\frac{e\dot{\mathbf{f}}}{6\pi c^3}\int a\rho_{R=a}\cos^2\beta dS$$

where α, β are the angles between **R**, and **f** and $\dot{\mathbf{f}}$, respectively. The surface integrals arise from the infinite discontinuity of $\nabla\rho$ at the surface, $R=a$.

By the use of Gauss' Theorem, the surface integrals may each be proved equal to the negative of the sum of the corresponding classical and extra-classical volume reactions, so that for any centrally symmetrical distribution of charge (which may be very different from the distribution designed by Bateman to secure equilibrium within the stationary electron[5]) the **f** and $\dot{\mathbf{f}}$ reactions vanish.

The vanishing of the **f** reaction is interpreted to mean that the mass is zero, and this is in agreement with the result in the final section where the case of uniform (or quasi-stationary) motion is treated. By introducing (in the last three of his papers[1]) new tensors to remove certain surface discontinuities in the components of T^e+T^s for the stationary electron, Bateman succeeds in rendering the mass different from zero—the actual value obtained, regardless of the way in which density varies with distance from the center, is three times the mass of a Lorentz electron with a uniform surface distribution. But the $\dot{\mathbf{f}}$ reaction remains zero. This result seems to indicate that radiation is impossible. When, however, the energy radiated by a point charge is considered, it develops[1] that the energy radiation vanishes, on the average, only for periodic motion.[6]

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[5] This distribution is obtained by putting $F^e+F^s=0$ inside the stationary electron. The advantage it enjoys over other distributions is that, when additional tensors are introduced, it leads to the exact relativistic relation between energy of the stationary field and rest-mass; without the additional tensors, this energy is zero, as well as the rest-mass.

Bateman, however, repeatedly states that the resultant body-force should be postulated to vanish everywhere. While this is in the spirit of relativity mechanics, it may be pointed out that for the immediate purposes of his analysis such a generality is not essential. In one of his papers (Messenger of Mathematics **52**, 122 (1922)) Bateman appears to make elaborate use of it, but his results there can readily be derived without it.

MOMENTUM OF THE FIELD FOR UNIFORM MOTION

That the mass of an electron is zero may also be inferred from the vanishing of the total momentum of the field of an electron in uniform (or quasi-stationary) motion. Bateman[7] obtains this result by using a transformation formula applying to tensors in the restricted theory of relativity. The momentum in question is thus shown to be a multiple of the total energy of the field of a stationary electron with his equilibrium distribution of charge, and this he has found to be zero.

While the argument can be modified so as not to involve any particular distribution of charge, another deduction requiring only central symmetry and using simpler relativity transformations may easily be made as follows: As can be shown[8] by changing to the reference system in which the uniformly moving electron is at rest, the electromagnetic momentum of its field is

$$\frac{\mathbf{v}}{c^2\sqrt{1-(v^2/c^2)}}\int(\nabla\Phi)^2\sin^2\theta dV \tag{5}$$

where the integral is extended over all space. Φ is the electrostatic potential due to the electron; dV is in polar coordinates so that θ has its usual significance, the polar axis being the direction of motion (velocity = $\mathbf{v}$) in the original reference system. It remains to calculate the extra-classical momentum, whose effective density is

$$\mathbf{G}^s=-\frac{2\mathbf{v}}{c^2v}\psi\frac{\partial^2\psi}{\partial x\partial t}$$

if the electron moves along the x-axis. The integration will again be carried out in the rest-system. As may be inferred from the definition of ψ and its invariance with respect to the Lorentz transformation, or may otherwise be proved directly, on changing the reference system ψ becomes Φ. Applying the Lorentz transformation to the differential coefficient and to the element of volume, we have for the extra-classical momentum

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[6] In his later papers, Bateman regards compensating negative energy radiation as a blemish in his theory. It is hard to gather from the context whether the tensor introduced in Messenger of Mathematics, **52,** 125 (1922) is meant to remove this blemish; if so, it does not serve its purpose, for calculation shows that it leaves the radiation of energy *in statu quo.*

[7] Messenger of Mathematics **53,** 147 (1924).

[8] L. Silberstein, Theory of Relativity, p. 214.

$$\frac{2\mathbf{v}}{c^2\sqrt{1-(v^2/c^2)}}\int \Phi \frac{\partial^2\Phi}{\partial x^2} dV$$

or, by symmetry,

$$\frac{2\mathbf{v}}{3c^2\sqrt{1-(v^2/c^2)}}\int \Phi\nabla^2\Phi dV \tag{6}$$

The trigonometric factor in the integrand of (5) may be replaced by 2/3. The sum of (5) and (6) is reducible to a surface integral by Green's Theorem, and this surface integral vanishes since Φ and $\nabla\Phi$ are finite and continuous at the surface of the electron and vanish at infinity.

The writer is greatly indebted to Professor Leigh Page of Yale University.

DEPARTMENT OF MATHEMATICS,
UNIVERSITY OF CINCINNATI,
September 14, 1925.

PHYSICAL REVIEW JANUARY, 1926 VOL. 27

THE DISPERSION OF THE OPTICAL CONSTANTS OF MERCURY

BY BRIAN O'BRIEN

ABSTRACT

Measurements were made on clean mercury surfaces prepared by the method of Roentgen as used by Wheeler. The optical constants were determined *for the range* 4358 *to* 3022*A* using the method of Jamin. Light from a mercury arc was dispersed by a quartz spectroscope of the Littrow type with a fused silicon mirror to reduce scattered visible light, and a phosphorescent screen or fluorescent solution was used in making the readings. The results for *refractive index n, absorption coefficient nk* and computed percentage *reflectivity R* at normal incidence, are as follows:

	4358	4047	3650	3130	3022
n	0.88	0.79	0.64	0.44	0.55
nk	3.47	3.40	2.97	2.53	2.25
R	77	78	78	79	70

The beginning of a region of transparency is apparently indicated at 3022A.

INTRODUCTION

THE effects of slight surface films on values obtained for the optical constants of metals by katoptric methods was pointed out by Voigt.[1] To eliminate such films Drude[2] attempted to specify a so-called "normal" surface, but large inconsistencies still remained in his results even among successive measurements on the same reflecting surface. Minor,[3] Meier,[4] Tool,[5] Ingersoll,[6] and Tate[7] have measured the optical constants of several of the metals from wave-length 2500A (Minor) to wave-length 2.25μ (Ingersoll). The values obtained have been collected by Wheeler.[8] He has pointed out that while different observers are in good agreement as to the amount and trend of the dispersion of the refractive index and absorption coefficient of a particular metal over a given region, they are not in good agreement on the absolute magnitude of these constants.

Wheeler[9] has measured the refractive index of several transparent liquids in contact with mercury by the reflection method, using Roentgen's[10] modification of the method suggested by Rayleigh[11] to clean the surface of contact between the mercury and the transparent liquid. Differing from those of previous observers, his results are very consistent, and agree in the third place with values of the refractive index of the same liquids determined by the usual methods. It would appear therefore, that all contaminating films at the metal-liquid surface were eliminated. He has also measured the optical constants of mercury in air over a portion of the visible spectrum.[12]

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[1] Voigt, Wied. Ann. **24,** Wied. Ann. **25,** (1885).
[2] Drude, Wied. Ann. **36,** 885; Wied. Ann. **39,** 481 (1899-1900).
[3] Minor, Ann. d. Physik **10,** 591 (1903).
[4] Meier, Ann. d. Physik **31,** 1017 (1910).
[5] Tool, Phys. Rev. **31,** 1 (1910).
[6] Ingersoll, Astrophys. J. **32,** 265 (1910).
[7] Tate, Phys. Rev. **33,** 321 (1912).
[8] Wheeler, Am. J. Sci. **35,** 491 (1913).
[9] Wheeler, Phil. Mag, **22,** 229 (1911); Am. J. Sci. **32,** 85 (1911).

The present investigation was undertaken to determine the optical constants of a mercury surface, cleaned in this manner, from the violet as far into the ultraviolet as feasible.

METHOD AND APPARATUS

The optical constants were determined by the usual method of measuring the ellipticity introduced into plane polarized light by reflection from the metal surface. The theory of the method has been given in detail by Drude.[2] If the incident light is plane polarized at an angle of 45° with the plane of incidence, if $\varphi\equiv$the angle of incidence, $\Delta\equiv$the phase difference after reflection between the components parallel and perpendicular to the plane of incidence, and $\psi\equiv$the azimuth of the restored plane of polarization, then if we write

$$\tan Q\equiv\sin\Delta\tan 2\psi\ ;\qquad \cos P\equiv\cos\Delta\sin 2\psi\ ;$$

$$S\equiv\tan\tfrac{1}{2}P\sin\varphi\tan\varphi\ ;$$

we get to a second approximation

$$n=S\cos Q(1+\sin^2\varphi/2S^2)$$

$$nk=S\sin Q(1-\sin^2\varphi/2S^2)$$

$$k=\tan Q(1-\sin^2\varphi/S^2)$$

where n is the refractive index and nk the absorption coefficient.

A spectrometer by the Société Genevôise, arranged so that the table could be swung to a vertical position to accommodate a horizontal mirror, was used as Jamin circle. The divided circle could be read to 20″ of arc. The polarizer and analyzer prisms were of the uncemented straight end type (Foucault-Glan), and their positions could be read to 0.1°. The compensator was of the Babinet-Soleil type, giving a uniform field instead of bands as in the original Babinet form. The movement of its wedge could be read to 0.0025 mm, which corresponded to an increment in Δ of 0.19° at the longest and 0.30° at the shortest wave-length used.

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[10] Roentgen, Wied. Ann. **46,** 152 (1892).

[11] Rayleigh, Phil. Mag. (5) **30,** 392 (1890).

[12] O'Brien and Wheeler, Phys. Rev. (2) **21,** 376, Abs. 26 (1923).

The source of light was a mercury arc in quartz, and a small quartz spectroscope of the Littrow type, which was built in this laboratory, was used as monochromatic illuminator. The reflector of the spectroscope was of fused silicon in place of the usual tin amalgam, the high ultraviolet and low visible reflectivity of the silicon reducing the effect of scattered visible light in the field.

The optical system is shown in Fig. 1. The mercury arc I was placed very close to the slit S_1 to eliminate a condensing lens. After passing through the analyzer the light was brought to a focus by the quartz lens L_3 on a fluorescent target F which was viewed from the side through an eyepiece E.

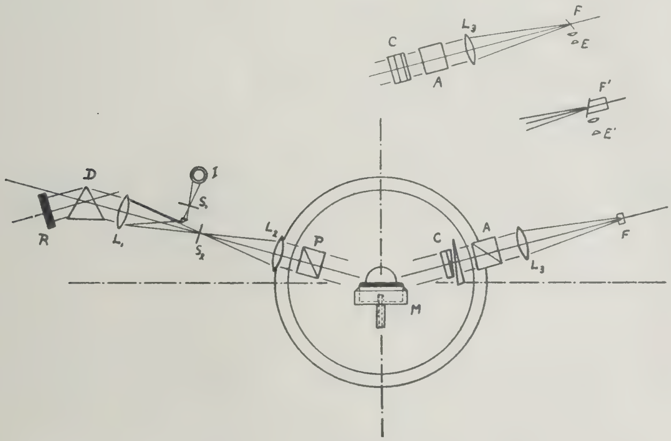

Fig. 1. The optical system.

A phosphorescent screen of very short period, and also a cell filled with a fluorescent solution were used. The screen consisted of varnished mica on which was dusted finely powdered potassium uranyl sulphate while the varnish was still "tacky." The cell was cylindrical, of glass, with a quartz end, and was filled with a very dilute aqueous solution of uranin, the sodium salt of fluorescein. The end of the cell on which was mounted the quartz window was cut obliquely so that the plane of the window made an angle of about 60° with the axis of the cell. The screen, when used, was placed as shown at F in Fig. 1. The cell, when used, was placed as shown at F' in Fig. 1, with its axis coincident with the optic axis of the lens L_3 and with the quartz window turned obliquely away from the eyepiece E' so that the solution immediately behind the window was viewed through the glass side-wall. The screen gave the more brilliant image, but the cell was preferable at certain settings where there was appreciable scattered visible light in the field. The maximum intensity of emitted light from both potassium uranyl sulphate and uranin lies at about the same wave-length as the maximum of visual sensitivity for faint illumination. This, together with their intense fluorescence, makes these materials particularly suitable for fluorescent eye pieces.

The whole system was enclosed in a light tight housing, and care was taken to exclude all light from the room. The eyes were rested in total darkness before each set of readings, and it was found possible to set the compensator and analyzer quite sharply to the position of quenching.

The surface cleaning apparatus was the one used by Wheeler,[8] with a few minor refinements. This has been described in detail by him. The mercury used had been electrolytically purified and distilled, and was the purest available. Precautions were taken to avoid contamination, the mercury coming in contact only with glass, "pure gum" rubber tubing, and iron, all of which were carefully cleaned. The mercury pool is shown diagrammatically at *M*, Fig. 1, the surrounding cup, upper and lower mercury reservoirs, etc., being omitted. Simply allowing mercury to run in through the nozzle in the center of the pool and overflow the rim, which was ground to a knife edge, produced an exceedingly clean surface, as shown by the consistency with which readings could be repeated on successive surfaces.

MEASUREMENTS

The lines of the mercury arc which were used were identified by taking the interval between them from a plate made with a spectrograph of similar dispersing system. The plane of polarization of the polarizing prisms was determined by reflecting light from a distilled water surface at the polarizing angle, the water surface having been cleaned by the method described above for mercury. The divided circles of the prisms were investigated for uniformity of scale. The compensator was calibrated over the full range of motion of its wedge at each wave-length used. The angle of incidence was made 74° 50′, which is close to the principal angles of incidence for mercury at the wave-lengths used, and was checked by two methods. Readings were taken with the polarizer both right and left of the plane of incidence in each series, and at both 0° and 180° quenching points along the full travel of the compensator wedge.

Observations were made in still air quite free from dust, and the mercury surface was cleaned every five minutes, although no change in constants could be detected in a surface standing as long as fifteen minutes. Measurements were repeated to within the probable error of observation over a period of several months, and it is believed that surfaces were obtained free from all contaminating films, the figures representing absolute values for the metal itself. The temperature of the room and of the mercury remained between 20.0° and 22.0°C throughout the period of observation.

The results obtained, together with the probable errors, are given in Table I and are shown graphically in Fig. 2. The values of n and nk were computed from the formulas given above, and the reflectivity at normal incidence, R, from the formula

$$R=\frac{n^2(1+k^2)+1-2n}{n^2(1+k^2)+1+2n}.$$

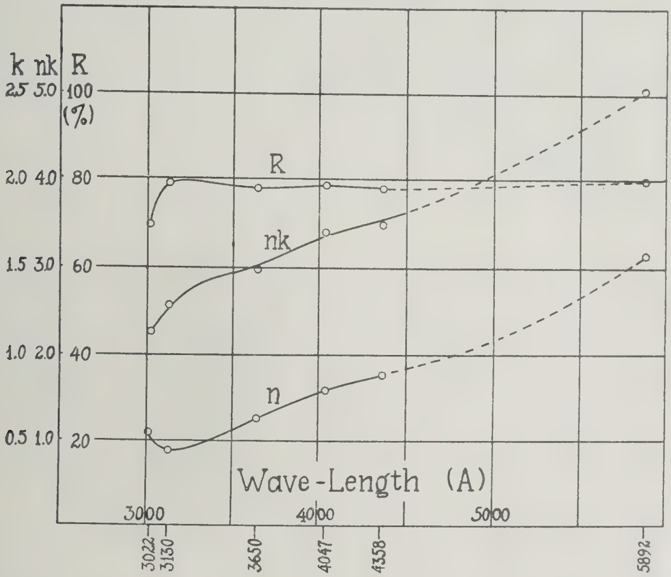

Fig. 2. The optical constants of mercury as a function of wave-length.

The figures in parentheses were computed from values of Q, P, and S, at wave-length 5892A, and for $\varphi=60°$, given by Wheeler.[8] He has also

TABLE I

Optical constants of mercury in air

λ	φ^0	Δ^0	ψ^0	n	nk	R(calc)
(5892A)*	(60.00)	(149.73±0.07)	(40.67±0.09)	(1.57)	(5.05)	(79.6)%
4358	74.83	92.2±0.18	38.3±0.09	0.88±0.01	3.47±0.01	77.1±0.4
4047	74.83	90.7±0.18	38.9±0.16	0.79±0.03	3.40±0.02	78.5±0.8
3650	74.83	83.3±0.15	39.5±0.10	0.64±0.01	2.97±0.01	77.7±0.7
3130	74.83	74.7±0.23	40.8±0.12	0.44±0.01	2.53±0.02	78.9±0.9
3022	74.83	69.4±0.48	39.4±0.16	0.55±0.01	2.25±0.03	69.7±1.4

* Results for this wave-length are from measurements by Wheeler.[8]

measured[12] the constants of mercury at wave-lengths 5770, 5461, and 4358A. The present result for 4358A is in good agreement with his. Settings were made at wave-length 4047A both by the direct visual method and with the phosphorescent screen, and agree within the probable error.

It is of interest to note from the trend of the curves at the shortest wave-length investigated, that we are apparently approaching a region of transparency similar to that found for silver at slightly longer wave-length.

The writer wishes to thank Professor B. B. Boltwood, from whom the uranium salts and fused silicon were obtained, Dr. G. C. Southworth, whose aid in reading and recording the polarimeter settings greatly increased the accuracy of the experimental work, and Professor Lynde P. Wheeler, at whose suggestion the problem was undertaken and who gave much helpful advice throughout the work.

Sloane Laboratory,
Yale University,
October 22, 1922.

BOOK REVIEWS

Popular Wissenschaftliche Vorlesungen. E. MACH. (Fifth enlarged and revised edition).—This collection of essays dedicated to the memory of Professor William James contains 33 papers which were delivered over a period of over fifty years by Professor Mach. Many of these have been translated and some have appeared in book form. They cover a wide range of subjects but, in the main, are concerned with the philosophical basis of Physics and of Science in general. Mach's philosophy of life is explained in detail and he again emphasizes many of the difficulties in our philosophical approach to Physics. There is not one of them which cannot be read with interest by the teacher of Physics; and those who are familiar with his books on Mechanics and Heat especially will recognize the great influence Mach has had in presenting in logical form the underlying facts of all branches of Physics, and making clear the hypotheses or postulates on which the science rests. Many of his concepts must, of course, be replaced in view of the changes brought into our philosophy by Einstein and others, but this fact does not detract from the importance of his work. Many of the essays deal with the connection between Physics and Psychology, or Physics and psychical phenomena. On the whole Mach's influence as illustrated by these papers is notable and is also of permanent value.—Pp. 628, Johann Barth, Leipzig, 1923. J. S. AMES

Chemistry in modern life. SVANTE AUGUST ARRHENIUS, Director of the Nobel Institute, translated by Clifford S. Leonard, former Fellow in Chemistry of the American Scandinavian Foundation.—Dr. Svante Arrhenius differs from most research men of the first rank in that he is both willing and able to write for the general reader. His theory of the electrolytic dissociation opened a new era in analytical chemistry, and he has been one of the leaders and rewarders of scientific investigation ever since. Yet he does not disdain to talk of "Chemistry in Modern Life" in nontechnical language.

Arrhenius is a humanist in the widest sense of the word, and he is interested alike in the theory and applications of his science, in its history and its everyday uses. His "Chemistry in Modern Life" which proved a popular book in Sweden and Germany, is now published in English as one of the Van Nostrand "Library of Modern Sciences." The translator, Dr. Clifford S. Leonard, who as one of the exchange fellows of the American Scandinavian Foundation worked under Arrhenius in the laboratory of the Nobel Institute in Stockholm, has done more than merely put the book into English words, for he has eliminated some of the material that was of local interest and substituted corresponding references to American chemical industries.

The author has contributed a special preface to the American edition in which he reiterates the warning that he has often voiced before, that the public should realize that the rapid expansion of modern civilization is due to the use of fossil fuels and the easily accessible ores, all of which are limited in amount, and that chemists must study the possibilities of developing new energy sources if our civilization is to be maintained. This pregnant paragraph from his preface is worth quoting entire:

> The material basis of our present civilization depends on the use of fossil fuel. But it has been calculated that the accessible fossil coals will be nearly at an end in about 1,000 years, and petroleum in about twenty years. If we do not find some new source of energy within a thousand years, humanity will fall back to a state of civilization similar to that about a century ago, while the number of inhabitants of our planet will have to diminish to a corresponding degree. Luckily we have the energy of the water-falls which will not diminish in a sensible degree in comprehensible time, unless we cut off the forests

on which the water reserve is more or less dependent. We must harness these falls to save as much as possible of our present material culture. But even when we have taken them into our service they cannot compensate for the loss of fossil fuels. Humanity stands, therefore, before a great problem of finding new raw materials and new sources of energy that shall never become exhausted.

In the end Arrhenius reverts again to the thesis with which he began and concludes with the Chemists' Commandment "Thou shalt not waste."

The volume contains a vast amount of information on industrial processes and the practical meaning of chemical reactions. For instance, the chapter devoted to "The Cultural Value of Silica" covers a wide range from the baked clay of the Stone Age to the recent revolution in architecture due to concrete. Arrhenius does not dodge any of the difficult reactions or technical details in the glass and porcelain industries, but collates his material with skill. He, of course, devotes special attention to "The Sources of Energy" throughout the world, and discusses the possibility of a greater use of wind motors and the invention of solar engines. A greater part of the book is devoted to inorganic chemistry and metallurgy, but the chapters on "Dyes, Perfumes, and Drugs," "Cellulose and Rubber" and "The Bread Question" are practical and interesting.—New York, D. Van Nostrand, 1925. $3.00. EDWIN E. SLOSSON

The Principles of Thermodynamics. GEORGE BIRTWISTLE. The purpose of this book is unusual in a treatise on thermodynamics, namely to sketch the broad general principles and the most important practical applications for such men as intended mathematicians, chemists, astronomers, and physicists, whose future scientific work may be expected to bring them into more or less intimate contact with thermodynamics. The book seems admirably adapted to this purpose. The treatment is simple and the general tone almost conversational. Casual references are made to an immense variety of topics of physical importance, so that the virgin reader must be impressed by the erudition of the author and fascinated by the vista opened to him. If, however, fascinated by this exposition, he decides to make a more serious study of thermodynamics, he will do well to supplement this book with some other in which the conceptual difficulties are more emphasized, and from which a mastery of the difficulties in practical applications may be obtained by the solution of problems.

A quite minor criticism, in which I happen to be personally interested, refers to my experimental determination of the properties of liquids at high pressures; it is said that various thermodynamic relations were "tested" by these experiments. In these experiments no attempt was made to test any thermodynamic formula, but the results of thermodynamics were freely used in making deductions from the data, which were thermodynamically independent.

Subjects not treated, which might well come within the scope of such a book are: the third law of thermodynamics, more extensive reference to applications in physical chemistry, and Saha's work on thermal dissociation in the stars.—Pp. 163, Cambridge University Press, 1925. 7s. 6d. P. W. BRIDGMAN

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE CHICAGO MEETING, NOVEMBER 27 AND 28, 1925

The 135th meeting of the American Physical Society was held at the Ryerson Physical Laboratory, Chicago, Illinois, on November 27 and 28, 1925. The President of the Society, Professor Dayton C. Miller, presided. Morning and afternoon sessions were held with an attendance of about two hundred. The Saturday morning session was divided into two sections.

On Friday evening the Society held an informal dinner at the Quadrangle Club, attended by sixty-five members and guests.

The regular meeting of the Council was held on Friday, November 27, 1925. The following were elected to membership: Vernon M. Albers, Frank C. Archambo, Jr., Eugene M. Bacigalupi, Carl I. Baker, Roland F. Beers, Norman C. Beese, J. G. Black, E. Bungartz, John F. Burns, Alvin B. Cardwell, R. A. Castleman, Jr., F. M. Clark, Palmer H. Craig, William H. Crew, W. D. Crozier, Richard C. Darnell, Myrl N. Davis, Raymond Davis, F. M. Defandorf, Arthur F. Dittmer, E. Gilbert Dymond, Charles K. Eckels, Paul G. Edwards, Alexander Ellett, W. A. Ellmore, Edgar N. Griscwood, Vernon Guthrie, I. J. Gwinn, Adolph Haberly, Thomas F. Hargitt, Jamison R. Harrison, Gaylord P. Harnwell, K. Horovitz, Arnim D. Hummell, Charles W. Jarvis, T. J. Jones, William J. Jensen, Ernest J. Jones, Varnakale L. Jones, Olaf M. Jordahl, J. P. Karbler, Burton A. Kingsbury, John Kralovek, George G. Kretchmar, John R. Loofbourow, Erwin F. Lowry, Eric R. Lyon, Walter A. MacMair, M. C. Magarian, Miles J. Martin, Harry B. Marvin, L. R. Maxwell, George E. Merritt, Warren W. Mutch, Nathaniel C. Norman, A. Ray Olpin, E. B. Penrod, Donald S. Piston, A. H. Poetker, A. Porilsky, W. E. Ramsey, Alfred M. Randolph, R. A. Rogers, Duane E. Roller, Addison M. Rothrock, II, Leone Sagui, Vesper A. Schlenker, Walter A. Schneider, Raymond S. Seward, H. M. Sharp, George R. Shaw, Henry Shore, Francis G. Slack, Kenneth O. Smith, Henry E. Stauss, Fenton V. Stearns, James D. Stranathan, Paul K. Taylor, Harold C. Urey, Carl P. Utterback, Calvin N. Warfield, Bertram E. Warren, Wallace Waterfall, Harold E. Way, Julian H. Webb, Harold A. Wheeler, Gerald W. Willard, Thomas S. Wilson, Y. H. Woo, Robert S. Wood, Lawrence H. Yingling.

The regular scientific session consisted of 60 papers (10 of which were read by title), abstracts of which are given on the following pages. An **Author Index** will be found at the end.

HAROLD W. WEBB,
Secretary

ABSTRACTS OF PAPERS

1. **Energy distribution between the modified and the unmodified rays in the Compton effect.** Y. H. Woo, University of Chicago.—Using small tubes of the Compton type and Soller collimators, reliable measurements of the intensity of the scattered x-rays were obtained from five radiators—paraffin, wood, carbon, aluminium and sulfur. In the case of each of the first four scatterers the Mo Kα rays were scattered at 60°, 75°, 90°, 105°, 120°, 135°, 150° and 165° with the exception that for aluminium no reliable result was obtained at 165°. The scattering with sulfur was observed only at 75°, 90° and 105°. The results show that the energy ratio of the modified to the unmodified line for a given radiator increases with increasing scattering angle, as predicted by Jauncey's theory (Phys. Rev. **25**, 314 and 723); but a comparison of the numerical values of the intensity ratio given by Jauncey for carbon and sulfur at 90° with the present results indicates that the theory overestimates this ratio. Experiments were also performed by keeping a lithium radiator in a lead cell filled with hydrogen. As far as they go, the results indicate that in the secondary x-rays scattered from metallic lithium the unmodified line in the Compton effect disappears.

2. **Separation of the modified and unmodified scattering coefficients of x-rays.** O. K. DEFOE and G. E. M. JAUNCEY, Washington University, St. Louis.—The methods of a previous paper (Proc. Nat. Acad. Sci., **11**, 517) for measuring the ratio of S_2, the modified scattering coefficient at a given scattering angle ϕ, to S_1, the unmodified scattering coefficient, have been improved. Instead of measuring the scattered intensities entering an ionization chamber set at ϕ before and after the transfer of a certain thickness of aluminum from a position P in the primary beam to a position Q in the scattered beam, we now keep the scattered intensity the same after the transfer as before by allowing more primary rays to fall upon the scattering block. This is done by means of a slit whose opening can be varied. A formula for S_2/S_1 is given in terms of the slit openings before and after the transfer of a known thickness of aluminum from P to Q and of the change of absorption coefficient of the modified rays in aluminum on scattering. A null method has been devised, in which two ionization chambers set at the same angle ϕ at opposite voltages are connected to the same electrometer. Aluminum is transferred from P to Q for one chamber but not for the other.

3. **A precision measurement of the change of wave-length of scattered x-rays.** H. M. SHARP, University of Chicago.—According to the quantum theory, the change of wave-length of scattered radiation is $\delta\lambda = h/mc\ (1-\cos\phi)$ where h is Planck's radiation constant, m is the mass of the electron, c the velocity of light and ϕ the angle of scattering. A test has been made when ϕ was 169°, using molybdenum radiation and paraffin as the scattering material. The scattered beam passed to a calcite crystal and slit attached to the x-ray tube and thence to the photographic plate. The observed value of $\delta\lambda$ is $(.04825 \pm .00017)$ A and the calculated value $(.04798 \pm .00009)$A. Using the data

of the experiment a value of the *mass of an electron* independent of e/m has been determined. This value is $(8.99 \pm .034) \times 10^{-28}$ g.

4. Theory of the intensity of scattered x-rays. G. E. M. Jauncey, Washington University, St. Louis.—The theory of previous papers (Phys. Rev. **25,** 314 and 723) predicts a value for the ratio of s_2, the energy of the modified x-rays scattered at an angle ϕ, to s_1, the energy of the unmodified x-rays. The theoretical value of s_2/s_1, however, is based on the assumption that the probability that an electron will scatter in a direction ϕ when it is in an orbital position M to scatter modified rays, is the same as that when it is in an orbital position U to scatter unmodified rays. This assumption is incorrect and, instead of giving s_2/s_1, the theory gives $p(\phi)$, the fraction of electrons which at any instant are in the M position, and $\left\{1-p(\phi)\right\}$ the fraction in the U position. The angular distribution of the intensity of the modified rays is then given by multiplying the right side of Eq. (27) of Compton's paper or of Eq. (21) of Jauncey's paper (Phys. Rev. **21,** 483 and **22,** 233) by $p(\phi)$. However, due to the invalidity of the above assumption, the angular distribution of the intensity of the unmodified rays is not given by multiplying the right sides of the above equations by $\left\{1-p(\phi).\right\}$

5. The disappearance of the unmodified line in the Compton effect. G. E. M. Jauncey, R. A. Boyd and W. W. Nipper, Washington University.—Jauncey's theory of the unmodified line (Phys. Rev. **25,** 314) requires the disappearance of this line at values of the scattering angle greater than that given by vers $\phi = 242\ \lambda_0^2/\lambda_s$, where λ_0 is the wave-length of the primary x-rays and λ_s is the K critical absorption limit of the scattering substance and both λ_0 and λ_s are given in angstroms. For the scattering of Mo Kα or Mo Kβ x-rays by carbon or by any element of higher atomic number, there is no real solution of the above equation and the unmodified lines are always present. However, for scattering by boron the unmodified Kα and Kβ lines should disappear at 147° and 117° respectively. We have accordingly scattered Mo x-rays by boron at about 145° to 150° and have examined the scattered spectrum photographically by means of a Sieman-Ross x-ray spectrometer. After a 60 hour exposure the modified Kα and Kβ lines show up plainly but the unmodified lines are either absent or are so faint that they escape detection. Further experiments are in progress.

6. The scattering and absorption of the gamma-rays of radium. H. M. Cave and J. A. Gray, Queen's University.—(1) Gamma-rays filtered through 2 cm of lead have a mass scattering coefficient equal to $0.102\ Z/A$, where Z is the atomic number and A the atomic weight of the material used. $(\mu/\rho)_{Pb}$ is 0.053. (2) Gamma-rays for which $(\mu/\rho)_{Pb} = 0.0475$ have been isolated. (3) The distribution of the radiation scattered from paraffin wax has been determined. (4) The results indicate that gamma-rays filtered through 2 cm of lead have an effective wave-length in the neighborhood of 0.012A. It must be stated, however, that the variation of scattering and absorption coefficients with wave-length is not known with sufficient accuracy for an estimation of this wave-length to be made with any degree of certainty.

7. The K series emission spectra for elements from atomic number 50 (Sn) to atomic number 83 (Bi). J. M. Cork and B. R. Stephenson, University of Michigan.—Using a spectrograph similar to that previously described except having a greater distance (75.593 cm) between slit and photographic plate, measurements were made upon the K emission spectra of all elements from Sn 50 to Bi 83 inclusive except 54(Xe), 61, 67 (Ho), 75, and 80(Hg). The wave-length values of the α', α, β and γ lines are given in every case except for the γ line of Bi 83. In addition the frequency numbers ν/R and $(\nu/R)^{1/2}$ are given. Variations with atomic number in the value of the regular doublet wave-length difference $d\lambda$ for the α' and α lines, are shown, together with irregularities in some of the outer energy levels of elements in the rare earth group.

8. **Theory of the continuous x-ray spectrum.** M. SANDOVAL VALLARTA, Massachusetts Institute of Technology.—A theory is presented, based on the following principles: (1) The continuous x-ray spectrum is due solely to stoppage of electrons on the anticathode; (2) emission takes place as light-quanta satisfying Bohr's frequency relation; (3) conservation of energy and of momentum hold for a system made up of impinging electron, anticathode atom and emitted light-quantum; (4) the impinging electron may or may not lose all its kinetic energy (the loss of energy is at random for different electrons); (5) the relation $m = m_0(1-\beta^2)^{-\frac{1}{2}}$ holds for both electrons and atoms; and (6) mass is equal to $h\nu/c^2$. Differences in electron velocities before impact are neglected, also possible changes in the potential energy of atoms. As may be seen, the continuous and the characteristic spectra are supposed to have a different mechanism of emission. One consequence that can be tested experimentally is that the sharp limit depends not only on the tube voltage but also on the direction of observation and on the anticathode material. This has already been pointed out by Bronstein. The effect is measurable only for voltages less than 1 kv and elements lighter than aluminum. Curves are given showing variation of expected effect for different voltages and different materials.

9. **Energy distribution in the continuous x-ray spectrum.** C. N. WALL, University of Illinois, (introduced by Jakob Kunz).—H. A. Kramers has given a theory which accounts for the main features of the energy distribution in the continuous x-ray spectrum as observed by H. Kuhlenkampff and others. The theory is based upon energy radiation processes which occur in a collision between a free electron and a positive nucleus, and upon ideas underlying Bohr's correspondence principle. In this paper the theory is simplified by considerations of both energy and angular momentum radiation processes which occur during a collision. The result obtained is essentially the same as that obtained by Kramers.

10. **Diffraction of x-rays in liquids.** G. W. STEWART, ROGER M. MORROW and E. W. SKINNER, University of Iowa.—Using the Kα radiation from a molybdenum target, the diffraction of x-rays was determined by an ionization chamber placed at varying scattering angles θ. The following are the experimental results: *By Morrow*: (a) Solid and liquid camphor at 21°C and 205°C respectively show the same location of intensity peaks, allowance being made for expansion. (b) Naphthalene, α-naphthol and β-naphthol, as liquids, each give a single broad peak which is roughly a mean of the peaks occurring with the solid state. These single broad peaks occur at temperatures close to the freezing point, also crystalline peaks persist to the melting point. *By Skinner*: (a) In each of the five normal saturated alcohols, methyl, propyl, hexyl, octyl and decyl, a single broad peak is accompanied by smaller ones indicating a larger "grating" spacing. The intensity curves are similar but shifted to smaller values of θ with the heavier molecule.—The above experiments are favorable to the interpretation of the phenomena as having an interatomic cause, probably the existence of crystal fragments giving low resolving power. All known data are favorable and none contradictory to this assumption of crystal fragments.

11. **Diffraction of x-rays by a ruled metallic grating.** R. L. DOAN and A. H. COMPTON, University of Chicago.—X-ray spectra may be obtained by ordinary optical methods if a grating of large constant is used, with sufficiently small glancing angles of incidence. It is necessary to work within the angle of total reflection, in which case the reflected beam is relatively quite intense. The expression for the wave-length is $n\lambda = \frac{1}{2}d(\alpha^2+2\alpha\theta)$ where θ and α are respectively the angles of incidence and diffraction. X-rays from a molybdenum target, made homogeneous by reflection from a calcite crystal, were allowed to fall upon a grating at a glancing angle of less than 10 minutes

of arc. In the best photographs three orders of spectra were obtained. Measurements of wave-length on the $K\alpha_1$ line gave: $\lambda=(0.707\pm.003)$A. Experiments carried out with a copper tube were hindered by lack of intensity but such calculations as could be made were satisfactory. More precise measurements on the $K\alpha_1$ radiation from these two elements are now in progress.

12. Lattice parameters and densities of Cu, Ag and W. Wheeler P. Davey and T. A. Wilson, General Electric Co.—If diffraction patterns of two strain-free crystals are taken on the same film, the crystals have the same equivalent center of diffraction if they are both diluted so as to have the same efficiency of diffraction. A review of diffraction patterns of Cu previously reported showed that this requirement had not been sufficiently met. New patterns have been taken (a) with the calibrating substance (NaCl) mixed with the Cu, and (b) with diluted Cu at one end of the specimen tube and NaCl at the other end. Both methods give 3.605A for the side of the unit cube. This gives a density of 8.95. A single crystal of Cu 3 inches long and 1 inch in diameter gave a density 8.953 by ordinary methods. This changes Patterson's values for Cr and Ti by 0.3 percent. Density measurements by ordinary methods on a large single crystal of Ag gave a density 10.481, agreeing with the previously reported value 10.49 by x-ray methods. New x-ray experiments on W using both methods of calibration confirm the previous result, side of unit-cube $=3.155$A; density $=19.32$. This value for W is consistent with the new value for Cu.

13. On some solutions of Maxwell-Lorentz equations which may correspond to Bohr's quantum postulates. N. Rashevsky, Westinghouse Electric and Manufacturing Company, East Pittsburgh, (introduced by Dayton Ulrey).—It is pointed out that the two postulates of the quantum theory, (1) the existence of accelerated electron motion without radiation, and (2) the emission of monochromatic radiation by a non-periodical motion of the electron, are incompatible not with the classical field equations themselves, but only with their solutions in terms of retarded potential. Using advanced potentials, solutions compatible with (1) have been obtained by G. Nordstrom and Leigh Page. A way of obtaining solutions compatible with (2) has been indicated by Lanzsos for a non-euclidian space. In this paper (a) the general mathematical conditions, which a solution must satisfy in order to be compatible with (1), are investigated; also (b) such a solution is actually constructed by adding to the retarded potentials other suitable chosen solutions of the homogeneous equations; and finally (c) by a similar method solutions are constructed, compatible with (2). It is investigated under what conditions the solution (b) can continuously pass into (c) and vice versa.

14. Transition probabilities and principal quantum numbers. Frank C. Hoyt, University of Chicago.—In calculating approximate values of probabilities of transition from the amplitudes in a harmonic analysis of the electric moment of the atom, the order of the harmonic "corresponding" to a given transition depends on the quantum numbers of the stationary states involved. Hence it would seem possible to determine these quantum numbers in doubtful cases by comparison of such computed values with those deduced from experiment. However, in the case of a single electron moving in an orbit of the penetrating type as in ordinary series spectra it may be shown from the harmonic analysis obtained elsewhere (Phys. Rev. **25**, 174, 1925) for such an orbit that the dependence of the amplitudes on the order of the harmonic is such that they are in reality functions only of quantities that may be found from the energies in the stationary states (effective quantum numbers) alone, together with the subordinate quantum numbers. The transition probabilities are thus independent of the assignment of principal quantum numbers. This question is of importance in view of recent attempts to draw conclusions as to the principal quantum numbers from experiments on the intensities, absorption, dispersion, or magneto-rotation of spectral lines.

15. Stripped oxygen. I. S. BOWEN and R. A. MILLIKAN, California Institute of Technology.—We have heretofore obtained and published the spectra of the stripped atoms of all the elements contained in the first two rows of the periodic table except oxygen and fluorine. We can now report the successful stripping of the oxygen atom and the location of the doublet corresponding to the first term of its principal series at λλ1031.98, 1037.69. The ionization potential is here 137 volts, a number higher than that possessed by any of the atoms thus far stripped, or indeed of any optical series thus far worked upon. We have also obtained the *pp′* group of the two electron system O_V, with such resolution as to clearly bring it out as a sextriplet instead of a quintriplet, and to fix the p_1p_2/p_0p_1 (Sommerfeld notation, Atombau p. 577) ratio for oxygen at 2.27, a ratio fairly close to the value shown by all two-valence-electron systems except beryllium.

16. The pp′ groups in atomic spectra. R. A. SAWYER, University of Michigan.—In order to explain the *pp′* groups in two-valence-electron systems, Wentzel, and Saunders and Russel have suggested that the second electron makes a *ds* transition, while Bowen and Millikan favor a *ps* transition. The present paper suggests as a more general relation that the *pp′* frequency is associated with the difference in frequency between the two lowest singlet levels in the spectrum concerned and with the difference in level between the two lowest doublet levels in the next spectrum (once more ionized atom). This may be a singlet *SP*, singlet *SD*, doublet $\sigma\pi$ or doublet $\sigma\delta$ transition. For certain two-valence-electron system spectra the *pp′* frequency is nearly a mean between the lowest singlet *SP* transition and the lowest doublet $\sigma\pi$ transition of the next system. From this relationship the location of the *pp′* group of ZnI has been predicted and the group identified. For three-valence-electron systems the *pp′* group is near the lowest singlet *SP* transition of the next system. The πX doublet of AlI has been identified. Numerical examples are given and the significance of these results discussed.

17. The spectrum of beryllium. R. F. PATON and W. H. SANDERS, University of Illinois.—The comparatively simple structure of the beryllium atom makes its line spectrum a matter of particularly great interest. However, due to its chemical and physical properties the knowledge of its spectrum is very meager. Fortunately the authors were able to secure from Dr. B. S. Hopkins a sample of beryllium-aluminum alloy formed in the preparation of pure beryllium. Samples of this alloy used as electrodes in a vacuum spark chamber, furnished a satisfactory source. The spectrum was photographed with a quartz spectrograph. Several satisfactory spectrograms have been obtained and the results tabulated from λ5200 to λ2000. The known lines of beryllium are the most intense on the plates. In addition to these there is a considerable number of new lines which have been ascribed to beryllium, since they occur on all the beryllium plates, but correspond to no recorded wave-lengths and are absent from spectrograms of impurities. More complete data now being taken should permit the classification of these new beryllium lines in series.

18. The absorption spectrum of manganese vapor. R. V. ZUMSTEIN, National Research Fellow, University of Michigan.—By heating the manganese in a small carbon tube to about 1600°C, absorption was observed at 31 lines. Grotrian had reported absorption at 6 lines. All of the absorptions are from manganese atoms in the normal state (1^6s term) and occur in groups of 1, 2 and 3 lines. Five absorption lines represent $1^6s-{}^6d'$ combinations for which the rule of inner quantum numbers is obeyed but the azimuthal quantum number changes by 2. Four lines are $1^6s-{}^8p$ combinations and twelve are $1^6s-{}^6p$ combinations. Some of the remainder are perhaps $1^6s-{}^4p$ and $1^6s-{}^2p$ combinations.

19. The Zeeman effect for the spectrum of flourine. G. HOWARD CARRAGAN, University of Chicago.—An electromagnet suitable for work on the Zeeman effect at high field strengths has been designed and constructed for the purpose of this investigation. Certain improvements in the technique of handling flourine have been instituted and a form of discharge tube has been devised which is suitable for giving the flourine spectrum under high field strengths. The red spectrum has been photographed in the 1st, 2nd and 4th orders of the 10-inch Michelson grating, and the Zeeman patterns of twenty of the brighter lines obtained. The analysis of these patterns with a consideration of the ratios of the intervals between the lines and the distribution of their relative intensities seem to indicate a quartet system. The principal and diffuse series term combinations have been located on this basis. The term combinations of other lines have been proposed and certain unexplained anomalies in the spectrum pointed out. Certain lines observed by Gale and Monk but not given in their published list of wave-lengths are cited.

20. The law of force and the size of diatomic molecules, as determined from their band spectra. Raymond T. Birge, University of California.—Assuming for the law of force of a diatomic molecule, in the vicinity of the equilibrium position, $F=k_1(r-r_0)+k_2(r-r_0)^2+$ etc., explicit expressions for the k's have been derived in terms of the constants of the usual *rotational* energy function for a *non-vibrating* molecule, $E_m=Bm^2+Dm^4+Fm^6$ etc., where m is generally a half integer. Values for the k's, from the *vibrational* energy function of a *non-rotating* molecule may be obtained from the work of Born and Hückel. Although the error is much greater when using rotational data, the two independent values of k_1 are found to agree on an average to two percent, for the initial and final states of the CN, CuH, N_2 and N_2^+ molecules. Dieke's explanation of the intensity anomalies of non-polar molecules requires a moment of inertia I only one-quarter as large as the older accepted values, and this in turn makes the value of k_1, from rotation only, just four times as large. Hence the above quantitative agreements, based on the older values of I, form conclusive evidence in favor of these older values.

21. The quantum analysis of the band spectrum of AlO (λ5200-λ4650). W. C. Pomeroy and R. T. Birge, University of California.—Using a new form of aluminum arc, spectrograms were taken in 1915 by one of us, in the second order of the large concave grating of the University of Wisconsin. These have now been measured and the (0,0), (1,0), and (0,1) bands of the blue and green group analyzed according to the quantum theory. Although the series lines of each band are concealed in the vicinity of the "origin," these points have been definitely located by an extensive and accurate verification of the combination principle. No other choice of origins gives even approximate verification. The necessary theoretical relations between vibrational and rotational energy constants enable the absolute values of the rotational quantum numbers to be established to ±0.02. They are exact half-integers. The origin of the (0,0) band (λ4842) is at $\nu_{\text{vac}}=20{,}635.3$, and the limiting values of the moments of inertia for initial (emission) and final states are $(46.01\pm0.04)\times10^{-40}$ and $(43.38\pm0.04)\times10^{-40}$ respectively. These bands have no Q branch, and the P and R branches consist of doublets of the violet CN type. The three bands measured have no observable perturbations. Additional theoretical relations are now being tested.

22. Effect of the type of source on the primary standard of wave-length. George S. Monk, University of Chicago.—Owing to its use as the primary standard of wave-length, it is of fundamental importance to know under what conditions of production, if any, the wave-length of the red Cd line 6438.4696 A, will vary. Accordingly, several sources have been studied by the use of the Fabry-Perot etalon and auxiliary grating dispersion. In agreement with the determinations of Hamy it is found that the electrodeless tube yields the same value as one with electrodes. The design of the tube and the type of discharge have no observed effect on the wave-length. The cadmium-filled carbon arc in vacuum gives the same value, but owing to greater intrinsic line width, the measurements from this source are attended by a larger error. Also, some interesting differences in intensity have been observed. The strongest visible line in the sharp singlet series, λ5154, is subject to measurements of the highest order of accuracy, but on account of its relative faintness is not desirable as a standard of wave-length.

23. **Greater dispersion in the extreme ultra-violet.** R. J. LANG and STANLEY SMITH, University of Alberta, (introduced by G. W. Stewart).—The construction and operation of an optical *vacuum-grating spectrograph* capable of accommodating a grating of two meters radius of curvature is described. Means are provided for introducing and removing the photographic plate as well as for altering the focus and inclination of the grating while the vacuum is maintained. *Doublet separations for* C_{II}. The following doublets in Fowler's series have been resolved. For $(2\pi_{1,2}-3\sigma)$, $\Delta\nu=64$ in the second order of the grating and 60 in the third order. For $(2\pi_{1,2}-3\delta)$, $\Delta\nu=64.5$ in 2nd order. For lines $\lambda=1335$ $\Delta\nu=65$ and lines $\lambda=1036$, $\Delta\nu=62$ showing that since the 1036 line belongs to C^+ probably 1335 does also. *Doublet separation for* Si_{III}. In this series the doublet $(3\sigma_{1,2}-4\pi)$ has a separation $\Delta\nu=153$.

24. **Coloring of glass in ultra-violet light.** C. L. CROSS, University of Iowa, (introduced by John A. Eldridge).—It is known that glasses containing manganese are tinted when subjected to x-ray or radioactive illumination and that the same phenomenon occurs when the glass is subjected to ultra-violet light. The phenomenon is closely related to phosphorescence. It is found that the effective light has a wave-length only slightly greater than 2900 (the absorption limit of the glass). Consequently the tinting is confined to very near the surface. The tinting is greatly hastened by heating. Two different colors may be obtained depending on temperature. At room temperature a brown color is produced which with time turns to purple. At 100°C the purple is produced at once. The reverse action (decolorizing) is accelerated by heat or visible light. A possible mechanism is suggested.

25. **The passage of protons and charged hydrogen molecules through gases.** A. J. DEMPSTER, University of Chicago.—Protons and charged hydrogen molecules with a slow velocity, corresponding to a potential difference of 300 to 900 volts, will pass through many molecules without being neutralized, contrary to what would be expected from the results with canal rays and α rays. Thus protons have been observed with their original charge after 9 collisions with hydrogen and 26 collisions with helium atoms, using the kinetic theory value of the molecular diameters. The rays were still observable, though scattered, when the number of collisions was four times as great as that just mentioned. Similar results hold in the case of charged hydrogen molecules. In air and hydrogen the penetration is somewhat less and the scattering greater. The velocities of the rays are small compared with the orbital velocity of the electrons, so that we may think of the rays as causing only an adiabatic distortion of the electronic arrangement while passing through, and producing no permanent alteration in the electronic distribution. There is no tendency for the helium to give up an electron since its ionization potential is 24.5 volts, and the energy of formation of the neutral atom or molecule considerably less.

26. **Collisions of the second kind in activated ozone.** H. D. SMYTH, Princeton University.—Last February a report was made concerning some experiments on collisions of the second kind between electrons and pseudo-excited atoms in iodine. Extension of the ideas on which that work was based suggests that if an electron collides with an activated molecule, the energy of activation or "critical increment" of the molecule may be converted to kinetic energy of the electron by a collision of the second kind, the

molecule, of course, being thereby reduced to a normal state. Experiments have been made on ozone decomposing into oxygen. With a simple arrangement of filament, grid, and plate, the current reaching the plate was measured as a function of a retarding field between the plate and grid. A constant small accelerating field was maintained between the filament and grid. If the process suggested above does occur, there should have been some electrons that had greater velocity than that due to the accelerating field alone, and such electrons should have been able to reach the plate after the retarding field was sufficient to cut off the main group. Some evidence of such high speed electrons was obtained.

27. Critical ionization potentials by positive ion impact in hydrogen. W. J. Hooper, University of California.—The experiments of several previous investigators were repeated in substance with apparatus designed to make it possible to distinguish between ionization and certain spurious factors which have made questionable much of the existing evidence relating to ionization by positive ion impact. A great many current-potential measurements and curves were obtained with a variety of electrical arrangements. The data and curves thus obtained present direct evidence (a) that the previously so-called ionization current is due to a secondary electron emission from the walls of the ionization chamber and not to ionization of the gas, (b) that this secondary electron emission is produced by the impact of the positive ions against these metal walls, (c) that either there is no ionization in hydrogen gas by the impact of positive ions accelerated by potential differences up to 925 volts, or that if this phenomenon exists, its effects are so small at relatively low pressures (.012 mm) that it is completely masked by secondary phenomena which make its detection by the ordinary direct methods problematic, and (d) that it seems possible that at relatively high gas pressures, ionization by positive ions might be an important factor with accelerating potential differences well within this same range of voltages.

28. An optical and electric study of the striated discharge in alkali vapors. A. J. McMaster, University of Illinois.—A study of the low voltage discharge in potassium vapor using a hot cathode of oxide-coated platinum wire is being made. When a small quantity of hydrogen is admitted to the discharge tube, beautiful striations of more than one color are produced. The distribution of the potential in and between the striations is measured by the exploring electrode according to the space charge method of Langmuir. A striation exhibits a number of well defined layers of different colors which are investigated by the spectroscope.

29. The distribution of potential in low voltage arcs. O. S. Duffendack and W. S. Kimball, University of Michigan.—Langmuir's sheath method was employed in measuring the distribution of potential in low-voltage arcs in hydrogen. The space a millimeter away from the filament is at practically the same potential as the anode. Thus there is a large fall of potential very near the cathode and only a small potential gradient over the remaining space. Only two potential states seem possible for a particular tube, a pre-arc state and an arc state. An oscillating arc is one in which there are rapid transitions between these two states. When a sufficient potential difference is applied between filament and anode of a soft detector or gas filled tube, an arc will strike unless the grid is made negative with respect to the filament; then an arc will not strike until the potential difference between the grid and filament is reduced to a characteristic value. After the arc strikes it becomes independent of the grid potential over wide limits. Such tubes have been used for locking circuits at critical instants and for peak voltmeters. After the grid potential reaches the critical value, an arc strikes in a very short time (order of one ten thousandth second) which becomes less with increasing anode potential.

30. Low-voltage characteristic in mercury vapor. RICHARD RUDY, Nela Research Laboratory.—The low-voltage mercury arc studied is produced between a surface of mercury and tungsten ribbons 1 to 2 mm wide and 1 to 3 cm long. As the electron emission is increased, the characteristic is gradually shifted towards lower voltages, and the arc finally becomes an abnormal low-voltage arc. Increasing the temperature of the ribbon lowers the voltage of the arc until strong currents pass at voltages lower than the first excitation potential. No oscillations are observed, since the characteristic is rising. Reverse fields may exist in the ordinary as well as in the abnormal low-voltage arc. These have been investigated by measuring the resistance of the arc by means of superimposed high frequency currents. With moderate heating of the filament the saturation current is well marked and is followed by a linear increase in current with the voltage, as ionization again sets in. The slope of this straight line is nearly proportional to the saturation current. With strong electron emission the ionization masks the saturation current. Currents of over half an ampere are possible with the anode less positive than the positive end of the filament. The effect of argon on this low voltage arc has also been examined.

31. Studies on active nitrogen. RICHARD RUDY, Nela Research Laboratory.—Afterglow was produced in a bulb containing nitrogen at a few mm pressure by passing a momentary discharge through the bulb. The rate of decay of the afterglow increased with increasing nitrogen pressure, so that the total light emitted became smaller and smaller. This effect was of the same order as the extinction of fluorescence in mercury when the density is increased. Argon, up to a few cm pressure, had little influence on the rate of decay. The decay was found to follow a bimolecular law for the first 100 seconds. The temperature coefficient of this reaction, between 20° and 130°, is much smaller than that of ordinary chemical reactions. For a bright afterglow all the bands of the first positive group of nitrogen were observed. In a bulb about 20 cm in diameter, afterglows lasting more than 15 minutes were obtained. The nitrogen molecule retains vibrational energy and therefore reacts quickly with other substances, or causes them to emit light, as if at high temperature. Band spectra excited by active nitrogen (particularly if the vibrational quanta are not too different) show vibrational energy as if at high temperature, whereas the rotational energy indicates low temperature.

32. On the discharge of electricity between equipotential plates. MASON E. HUFFORD, Indiana University.—A study has been made of the glow discharge of electricity between a perforated cathode and a connected auxiliary electrode. The dependence of the presence of the discharge upon pressure range was determined with aluminum electrode and various gases, air, oxygen-coal-gas, hydrogen-coal-gas, oxygen, hydrogen and helium. Experiments showed that electrons are evolved from the metal surface behind the cathode and these neutralize the canal rays. Experiments were made to show the relation of total voltage on the discharge tube to the current from cathode and auxiliary plate. Potentials at points in the glow region were measured by the probe method. The change of potential of a fixed point in the glow with change of pressure was tested. Study was made of the glow potentials using copper as cathode and again using gold as cathode. Potentials were measured when the walls of the tube were coated with sputtered metal and the discharge consisted of a glow only. Comparison was made of the fall of potential in the glow region and the cathode fall of potential obtained by other experimenters.

33. Mobility of the ions in the corona discharge. W. M. YOUNG, University of Illinois, (introduced by Jakob Kunz).—The mobilities of the ions generated in the direct current corona discharge have been directly measured. Gas, moving with a uniform velocity, has been ionized in a cylindrical corona tube and then passed into an ion chamber consisting of a hollow cylinder with electrodes along the axis. The ion current to the last electrode, when plotted as a function of the cylinder potential, exhibited maxima which indicated the formation of groups of ions. A large number of groups were obtained whose mobilities, for oxygen, nitrogen, and carbon dioxide were all less than .716 cm/sec/volt/cm, ranging down to 10^{-5} cm/sec/volt/cm. Nearly all mobilities were found less than 10^{-2}, the ions apparently being generated in about equal numbers, except that now and then a greater number of a certain mobility were formed. If it can be assumed that the charge determines the mobility of the ion, evidence can be found of ions which contain different charges. However, if mass is the determining factor, then ions may be picked out having the same charge but whose mobility varies inversely as the square root of the molecular weight. The fact that the ions all possessed small mobilities seems to indicate that J. Kunz made the correct assumptions when he calculated the average value from the experimental determination of the pressure increase in the d.c. corona.

34. Geiger counting chambers. C. W. HEWLETT, General Electric Co.—A study of Geiger counting chambers has been made, with the object of throwing some light on the mechanism by which radioactive rays register themselves in this type of apparatus. Evidence has been obtained suggesting that, in order to be registered, a radioactive ray must pass through a conical region extending from the point to the walls of the chamber. The extent of the base of this conical region may be very small and located on the end closing the chamber, or it may be large, covering the whole end of the chamber and even part of the side walls, depending upon the distance of the point from the end of the chamber. Examples are given of the determination of small amounts of radioactive matter mixed in relatively large amounts of other matter.

35. Shot-effect of electrons produced by impact ionization. ALBERT W. HULL and N. H. WILLIAMS, General Electric Company.—A two-electrode tube with pure tungsten filament was filled with argon to a pressure of .04 mm. The temperature of the filament was adjusted to give .003 m-amp. emission and the plate voltage raised until this emission current was multiplied thirty fold by ionization, giving a total current of 0.1 m-amp. The shot-effect was found to be exactly the same as for pure temperature-limited electron emission. This result would be in harmony with the hypothesis that ionization is effected in two steps, namely, absorption of energy from the impinging electron by the atom as a whole and subsequent emission of an electron after a brief, but random, interval. Such a process would account for the observation of Dushman and Found (Phys. Rev. **23**, 734, 1924) that the ionization in different gases is proportional to the total number of electrons in the molecules of the gases. A much larger shot-effect would be expected on the conventional theory of instantaneous emission, which assumes two low velocity electrons leaving the atom together as the result of an ionizing collision. It is possible, however, that some modification of this theory could account for the observed result.

36. The "reflection" of electrons from the anode of a Coolidge x-ray tube. W. R. HAM and MARSH W. WHITE, Pennsylvania State College.—Some of the electrons impinging on the anode of an x-ray tube are "reflected" to other portions of the tube. The ratio of the number reflected to the total number was measured quantitatively and found to be surprisingly large. The method employed was to measure the energy input into a water-cooled tube from a d.c. source and the heat received at the anode. The latter was obtained by using a flow calorimeter method. In a previous paper (Phys. Rev. **23**, 777, 1924) the writers described experiments which proved the equivalence between the energy input into an x-ray tube and the heat which is ultimately produced. Consequently the fraction of the electrons which are reflected is the ratio of the difference between the total energy and the heat generated at the target to the total energy input. The data indicate that the percentage of reflected electrons rises from approximately 15 at 2 kv to

25 at 5 kv and then falls off to 13 at 20 kv. These data were taken with a current of 10 m-amp. The experiments are being continued to study the variation of the reflection coefficient with other factors.

37. The role of the Faraday cylinder in the measurement of the velocities of the electrons emerging from small apertures. Ernest O. Lawrence, National Research Fellow, Yale University.—The experiments of Lehmann and Osgood (Proc. Cam. Phil. Soc., **22,** 731) led to the conclusion that a large fraction of the electrons emerging from small apertures have velocities less than the velocity corresponding to the applied voltage. However, the efficiency of the Faraday cylinder was not experimentally investigated. Present experiments with a Faraday cylinder of variable dimensions have shown that the observed apparent lack of homogeneity of velocities of the electrons is very definitely a function of the cylinder, indicating that a considerable part of the apparent inhomogeneity is merely due to a re-emission of electrons from the cylinder. These experiments show that Faraday cylinders in general are not as efficient absorbers as is usually assumed. This conclusion is further illustrated by the experiments of J. T. Tate (Phys. Rev. **17,** 395, 1921) who found that the most efficient Faraday cylinder he designed had an absorption coefficient of about .95.

38. Thermionic work function and space charge. J. Slepian, Westinghouse Electric and Manufacturing Company, East Pittsburgh, Pa.—Work function and space charge are separated on the basis that work function is microscopic in nature and space charge macroscopic. The work function then varies with electron space density, becoming zero or negative if the electron space density is sufficiently high. For an electrode in contact with a completely ionized gas at atmospheric pressure, the work function is reduced by about 0.6 volt.

39. Thermionic and evaporation characteristics of adsorbed films of caesium on tungsten. J. A. Becker, Bell Telephone Laboratories, Inc.—When a tungsten filament in caesium vapor is heated above a critical temperature T_c of 800°K, every atom that strikes evaporates as a positive ion. When the temperature T is lowered to 600° K, the caesium deposits, the electron current increases, comes to a sharp maximum at t_m seconds, decreases and later becomes steady. This shows that a certain number N_0 of caesium atoms produce an optimum activity. If the initial $T > T_c$ and the final $T < 600°$, t_m depends only on the positive ion current i_p. Hence above T_c the filament is bare if we draw positive ions; and below 600°K every atom that strikes sticks, at least until N_0 have stuck. If i_p is changed by varying the bulb temperature, $i_p \times t_m$ remains constant. From the value of this constant, $N_0 = (3.9 \pm .2) \times 10^{14}$ atoms/cm², which indicates that at the optimum the caesium is closely packed and has its atomic rather than its ionic diameter. Varying the initial conditions before lowering T shows that if the plate is negative both atoms and ions evaporate, while if it is positive only atoms evaporate. The atomic rate of evaporation increases with the fraction of the surface covered, whereas the ionic rate decreases.

40. Emission of positive ions from hot tungsten filaments. R. L. Kenworthy, University of Iowa, (introduced by John A. Eldridge).—Jenkins has shown that when the filament of a Coolidge tube is made very hot, positive ions are emitted. If heated for some time with reversed potential (which kept the positives from leaving the filament), the available positive ions appeared to accumulate so that when later an attracting field was applied an abnormally large positive emission was observed for several minutes. Using a special two element tube the phenomenon was further studied. In general Jenkins' results were confirmed. It was found that the proportion of the evaporated atoms which carried a positive charge was 1 in 1600.

41. Investigation of photo-electric valve coated with potassium. V. M. Albers, University of Illinois.—The tube used by Tykociner and Kunz has been studied more thoroughly. In the case of a transparent deposit on the connecting tube, curves are given showing the current through the tube when illuminated, I_l, and when dark, I_d. The ratio I_l/I_d reached a minimum at 40 and at 300 volts. The difference reached a maximum for a potential difference of 200 volts. The current increased linearly with light intensity at first and then less rapidly, approaching a saturation value. With an opaque film of potassium, illuminated through a window, the current increased in proportion to the voltage to 1000 volts and also in proportion to the light intensity. Evidently the thicker film gave the more efficient valve. Tests with dispersed light showed that with both transparent and opaque films, the current per unit energy decreased rapidly with increasing wave-length, reaching zero at between 520 and 540 $m\mu$. In explanation of these effects it is suggested that photo-electric emission from the film reduces the accumulation of electrons on the wall which tends to stop the current through the tube by electro-static repulsion. However, this does not explain the variation of the effect with wave-length.

42. The electrical conductance of the halides of sodium. T. E. Phipps, W. D. Lansing, and T. G. Cooke, University of Illinois, (introduced by Jakob Kunz).—The electrical conductance of the halides of sodium in the solid state was measured over a wide range of temperature. The powdered crystals were compressed under high pressure to semitransparent disks. In the case of NaCl, the conductance of this disk agreed very well with that of a natural crystal. A relation between conductance and temperature was derived theoretically and found to be $\kappa = ce^{-\epsilon/kT}$, where κ is the conductance, and ϵ is the energy of liberation of an ion in the lattice. Then $\epsilon = -kd \log \kappa/d(1/T)$ and ϵ can be calculated from the slope of the log κ, $1/T$ curve. Experimentally, each salt showed two distinct slopes, that at higher temperatures being approximately twice that at lower temperatures. A tentative explanation suggested for this behavior is that the positive ion alone conducts at lower temperatures and both ions at higher temperatures. It was found that for each sodium halide the energy of liberation of an ion in the lower temperature range was approximately 39 times the natural quantum of the crystal as derived from specific heat data.

43. Measurements of high frequency amplification with shielded-grid pliotrons. Albert W. Hull, General Electric Company.—Further tests have been made with the tubes previously described (abstract, Phys. Rev. **23**, 299, 1924). The distinguishing feature of these tubes is that they are made as nearly unidirectional as possible by thorough electrostatic shielding between the control-grid and plate. The shielding is accomplished internally by means of an extra grid between control-grid and plate, maintained at a constant positive potential, and externally by appropriate arrangement of supporting and leading-in wires and the use of grounded conductors. In this way it was found possible to reduce the effective capacity between control-grid and plate to less than .01 e.s.u. The most interesting application of these tubes is voltage amplification at high frequencies. Amplification measurements were made at 50, 1,000, and 10,000 kilocycles. At 50 kc the voltage amplification per stage was 200. At 1,000 kc each tube amplified 40-fold, and 4 in series gave a total voltage amplification of 2 million. This is shown to be the maximum amplification that can be usefully employed at any frequency, because of the presence of shot-effect. At 10,000 kc each tube amplified 7-fold, and 5 in series gave 10,000. No oscillations or other evidences of feedback were observed at any frequency. The use of *negative plate resistance* was found to be advantageous for cascade amplification with low battery voltage, and for single tube operation.

44. Measurement of the series resistance of a condenser at radio frequency. Charles D. Callis, Indiana University, (introduced by R. R. Ramsey).—The variable condenser is placed in a radio frequency (10^6 cycles) circuit with a coil made of fine wire with approximately the same high frequency and d.c. resistance. The resistance of the circuit is measured by the well known resistance variation method. The resistance is then measured with a second coil exactly like the first replacing it, and again with the two coils placed in series opposition so as to have the same inductance as that of one coil. From these three readings the resistance of the coils and the resistance of the condenser can be determined. It is found when the coils are made of fine wire that the computed resistance of the coils is the same as their d.c. resistance. Since the computed resistance is the d.c. resistance the assumption is made that the resistance of the coils is independent of position and constant, and that the computed resistance of the condenser is the true resistance. A number of sets of coils were made in order to obtain the condenser resistance at various dial readings. These values plotted against the reciprocal of the capacity give approximately a straight line.

45. **The high frequency resistance of condensers in series.** R. R. Ramsey, Indiana University.—In attempting to get a check on the work of Charles D. Callis (preceding abstract) it was discovered that if two condensers of the same general type were placed in series in a resonant circuit the resistance of the two condensers in series was approximately the same as the resistance of a single condenser when placed in the same resonant circuit. This is found to be a direct consequence of the ordinary law of resistances in series if the resistance of a variable condenser varies inversely with the capacity of the condenser.

46. **Linear amplification of galvanometer deflection by the photo-electric cell.** F. E. Null, University of Illinois.—Dr. Jakob Kunz suggested a method whereby the deflection of a moving mirror system may be amplified linearly by reflecting a beam of light from the mirror to a triangular slit in front of a photo-electric cell. This method has the advantage that the photo-electric cell has no lag. It may therefore be used to secure linear amplification of even short period instruments, such as the siphon recorder used in ocean cable signal reception.

47. **Electricity and Newton's third law of motion.** John A. Eldridge, University of Iowa.—Newton assumes action at a distance and asserts that the action and reaction act in opposite directions on the same line. The "magnetic forces" between two neighboring conductors violate this law, having parallel but not coincident lines of action. The contradiction is in part only apparent because "magnetic forces" are not strictly forces. The terminology is unfortunate since it misleads the student. The actual forces between two charged masses moving in a plane are always in this plane. Insofar as they are directed along the *line joining* the centers of charge they accord with Newton but there is usually a component in the *direction of motion* which is not Newtonian. This situation is usually summarized by saying that the electrical field is not derivable from a potential. While not agreeing with Newtonian mechanics, electrical phenomena are of course in good accord with relativity mechanics.

48. **The role of magnetism in valence.** E. H. Williams, University of Illinois.—The formation of chemical bonds by electric forces is difficult to reconcile with the Bohr atom. It has been suggested that valence may be due to magnetic forces produced by electronic orbits. The *magnetic susceptibility of odd and even molecules* (molecules containing an odd or an even number of electrons) has now been measured. Four substances containing both odd and even molecules have been tested. Two of these substances, compounds of copper and chlorine, changed from paramagnetic for odd molecules to diamagnetic for even molecules and the other two, compounds of manganese and cobalt, while strongly paramagnetic for odd molecules, became less paramagnetic for even molecules. This was especially noticeable in the case of cobalt compounds which de-

creased more than ten fold. Two oxides of both tin and lead were also examined. Since the atomic numbers of both of these elements are even, the oxides form even molecules. In all four cases the substances were diamagnetic. While conclusions cannot be drawn from the limited number of substances worked with, it is interesting to note that in all cases substances that are weakly paramagnetic for odd molecules become diamagnetic for even molecules and substances that are strongly paramagnetic for odd molecules become less paramagnetic for even molecules.

49. Temperature coefficient of magnetic permeability of sheet steel. THOMAS SPOONER, Westinghouse Research Laboratory, East Pittsburgh.—The temperature coefficients of magnetic permeability as a function of maximum induction and maximum magnetizing force are given for commercial sheet steel such as is used in electrical apparatus. The temperature range is from −20°C to +46°C. Three grades of material were tested having a silicon content of approximately 0.9, 2.2 and 4 percent, respectively. The average temperature coefficients have a negative sign for all inductions for the high silicon steel but for the low and medium silicon steels the coefficients are positive for the low inductions and negative for the high. The maximum negative temperature coefficients occur at about 10 kilogauss, which is appreciably higher than the inductions corresponding to maximum permeability.

50. J. W. Fisher's experiments and the possibility of magnetization by rotary fields. S. J. BARNETT, Carnegie Institution of Washington and California Institute of Technology.—In two recent investigations, with negative results, J. W. Fisher has looked for longitudinal magnetization of ferromagnetic cylinders in a cross magnetic field rotating in a plane normal to their axes. The present paper criticizes Fisher's theory, showing that the magnetization calculated by him should be multiplied by a factor approximately three halves the ratio of the cross magnetization to the saturation magnetization, thus reducing it very greatly and making the effect, if existent, undetectable under his experimental conditions. Another investigation of this effect, which is closely related to that of magnetization by rotation, now long established, is in progress here. A magnetic field, approximately uniform throughout a certain toroidal region and with intensity normal to the generating circles of the toroid, is produced and rotated by a two-phase current system. The toroid is filled with a ring, circular in cross-section, of fine permalloy wire surrounded with symmetrical coils in circuit with a galvanometer, whose throw is read when the rotation is reversed. This arrangement takes full advantage of permalloy's enormous susceptibility and eliminates disturbances due to fluctuations of the earth's field; and it is hoped that the elimination of other disturbances will make a conclusive investigation of the effect possible.

51. Torque on revolving cylindrical magnet. A. L. KIMBALL, JR., General Electric Co.—In a paper recently published in the Physical Review by Zeleny and Page, it was shown that the explanation often given of the cause of electromagnetic rotation of a cylindrical magnet with a side arm dipping into an annular trough is incorrect, but that by taking account of the reaction between the flux and current both in the magnet and in the side arm a good check between experiment and theory can be obtained. In the present paper it is shown that the experiment can also be explained by regarding the torque as arising from the reaction between the current in the part of the circuit external to the magnet, and the magnetic field, thus avoiding the necessity of thinking of the torque as arising from a reaction between current and field *both* carried by the suspended magnet, as assumed by Zeleny and Page. Both theories lead to the same law of torque.

52. The vapor pressure of solid sodium amalgams. FRANKLIN E. POINDEXTER, Washington University, St. Louis.—A Buckley ionization gauge was used to measure the vapor pressure of eight sodium amalgams ranging in concentration from 1:1 to 15:1 mol ratio of Hg to Na. The vapor pressure of each amalgam was measured at a number of temperatures which were determined by means of a platinum resistance thermometer. The pressures measured varied from approximately 10^{-8} mm to 10^{-3} mm over a maximum temperature range of from $-56°$ to 90°C. The log p vs $1/T$ graphs for the different amalgams were found to be approximately straight lines. The heats of reaction were calculated by means of the Van't Hoff reaction isochore, the pressures at different temperatures for these calculations being taken from the log p vs $1/T$ graphs. These heats of reaction varied from 15000 cal. in the case of the amalgams rich in Hg to 14,000 cal. for the 2:1 amalgam. This small heat difference over such a wide range of concentrations indicates that most of the heat of reaction between Na and Hg is liberated in the formation of the initial compounds.

53. **Variation of the coefficient of viscosity of air with the relative humidity.** J. C. Stearns, University of Chicago, (introduced by H. G. Gale).—The coefficient of viscosity of air with various relative humidities was measured by the concentric cylinder method. The presence of water vapor decreased the viscosity at all pressures. At atmospheric pressure the viscosity was reduced one third percent by saturating the air. At a pressure of 14 mm, the viscosity was reduced by 35 percent of its value when moisture was introduced.

54. **Transmission of sound by masonry partitions.** Paul E. Sabine, Riverbank Laboratories.—The reduction of the intensity of sound in transmission from room to room by way of partition walls of masonry was measured by the reverberation method. Eighteen tones, covering the pitch range from 128 to 4096/sec. were employed. Tests were made on walls 50 square feet in area, built into a doorway between two rooms entirely separated structurally. Eighteen walls, including the common types of permanent partitions were tested. The structural stiffness of the partitions was also determined by measuring the yielding of the mid-point under a small excess of atmospheric pressure on one side. For a single tone, the results of the tests were not interpretable. The average reduction over the whole tone range, however, proved to be independent of the structural stiffness of the partition and of the particular material employed and to be a function only of the mass per unit area of the partition considered as a whole. For masonry partitions under the test conditions ranging in weight from 10 to 45 pounds per square foot, the reduction of sound intensity in transmission is given very approximately by the equation $I/i = .593$ (Wt. in pounds/Area in sq. ft.)$^{5/2}$

55. **Transmission of sound by double-wall partitions.** Paul E. Sabine, Riverbank Laboratories.—The average reduction of intensity of sound in transmission by a single wall of gypsum tile was measured over the frequency range, 128 to 4096/sec. A second wall of the same weight and material was built without any structural connection and with an intervening air space of 2 inches between the two walls. The effects of structurally bridging and of filling this space with different materials were determined by measuring the transmission of sound by these structures. The following ratios of intensities, upon opposite sides of various composite walls of this type were obtained: single wall, 420; double wall bridged with wood, 10,300; double wall, sawdust filled, 8,700; double wall, slag filled, 11,300; double wall, felt filled, 31,000; double wall, completely separated and without filling, 32,000. The conclusion is drawn that the bridging action of a filler of absorbent material more than offsets the reduction of acoustical energy due to absorption by such a material.

56. **The action of acoustic wave-filters in solids.** H. F. Olson, University of Iowa, (introduced by G. W. Stewart).—Quantitative measurements of transmission in solid filters composed of brass cylindrical masses attached to a brass rod conduit, have been

made, and those in which the branches are cylindrical masses of like diameters and lengths show the following results. The application of the formula for low-frequency-pass filters in fluids was found possible provided the inertance of the branch is made equal to 0.75 of the volume and the capacitance of the branch 8.5×10^{-13} of the volume. The increase in volume of the branch, the increase in distance between the branches, and the appearance of the additional bands are all in accordance with the formulas for low-frequency-pass-filters. The physical action of the filter is very complicated but the above empirical relations indicate that a simplified theory of the action can be secured.

57. Optimum reverberation in auditoriums. F. R. WATSON, University of Illinois. —One of the necessary considerations in designing or correcting the acoustics of an auditorium is to secure conditions that will insure an optimum time of reverberation. A number of publications have dealt with this question, but from somewhat different standpoints. The writer has attempted to discuss these results on a common basis to show any differences that may exist.

58. Anomalous action of the Rayleigh disk. CHARLES H. SKINNER, Ohio Wesleyan University.—The turning moment on a Rayleigh disk when used to compare sound intensities is usually considered as proportional to the intensity and in such a direction as to set the disk more nearly at right angles to the axis of the resonator in which the disk is mounted. For certain short wave-lengths, however, the turning moment is reversed, and the disk tends to take up a position parallel to the axis of the resonator. The longest wave-length for which this occurs is approximately two times the diameter of the disk, the exact value depending on the relative dimensions of the disk and resonator.

59. The practical importance of relativity. JOHN A. ELDRIDGE, University of Iowa.—The restricted theory of relativity is usually considered recondite, without *practical* application. It is true that Newtonian mechanics are sufficiently accurate in other engineering applications, but not in the field of magnetism the existence of which is an indication of the breakdown of classical mechanics. In an electrical age it is hardly possible to consider relativity as an impractical refinement upon the Newtonian mechanics.

60. The isotopic composition and the atomic weight of terrestrial and meteoric chlorine. WILLIAM D. HARKINS and S. B. STONE, University of Chicago.—Accurate determinations of the atomic weights of meteoric and terrestrial chlorine indicate that this element has the same isotopic composition in the meteorite as on earth, which is favorable to the hypothesis of Harkins that the percentage of isotopes in elements is determined at least largely by the relative stability of the different types of atoms. The average atomic weight on earth of the meteorites is found by these determinations to be 35.457_6, which indicates 77.13 percent of the light isotope and 22.87 percent of the heavy, provided the atomic weights of the separate species are exactly 35 and 37. The table listed below gives in parentheses the number of determinations and the values represent the ratio of silver-chloride to silver, found by direct weighing, with the probable errors calculated by the method of least squares.

(7)	Apatite	1.32867_4	±	0.0000033
(7)	Wernerite	1.32867_4	±	43
(7)	Hydrochloric acid	1.32867_4	±	43
(21)	Terrestrial	1.32867_4	±	31
(7)	Meteoric	1.32868_0	±	47
(28)	Meteoric and terrestrial	1.32867_6	±	23
(8)	Sodalite	1.32868_0	±	67

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THE

PHYSICAL REVIEW

THE DISTRIBUTION OF ENERGY BETWEEN THE MODIFIED AND THE UNMODIFIED RAYS IN THE COMPTON EFFECT

By Y. H. Woo

Abstract

Intensity ratio of modified to unmodified scattered x-rays as a function of scattering angle.—Using small tubes of the Compton type and Soller collimators, reliable measurements of the intensity of scattered x-rays were obtained from five radiators—*paraffin, wood, carbon (graphite), aluminium and sulfur.* An ionization spectrometer (ethyl bromide) with a large calcite crystal was employed. Since the wave-length range investigated was small, the relative energy of each spectrum was obtained, to a close approximation, by integrating with a planimeter the area under the ionization curve which represented the line. The results of this measurement are as follows:

φ	R(paraffin)	R(wood)	R(carbon)	R(aluminium)	R(sulfur)
60°	2.29	1.19	1.08	0.46	....
75	3.10	1.85	1.31	0.74	0.25
90	4.69	2.73	1.45	0.91	0.42
105	5.16	3.21	1.82	1.23	0.67
120	5.49	4.57	2.26	1.45	....
135	6.52	5.38	3.42	2.11	....
150	6.98	6.21	4.05	2.52	....
165	7.47	7.00	4.86	....	....

where φ represents the scattering angle and R the intensity ratio of the modified to the unmodified line. The values of R increase with angle of scattering for a given element in the general manner predicted by Jauncey's theory, but the numerical values given by the theory are 20 to 50 percent too large. For a given angle, the values of R increases as the atomic number decreases, being greatest for paraffin which contains relatively more hydrogen than does wood. Experiments were also performed with a *lithium* radiator kept in a lead cell filled with hydrogen, on which two mica windows (about 0.005 mm in thickness) were provided so that one of them allowed the primary ray to fall on the scatterer and the other permitted the secondary ray to pass into the collimator. With a scattering angle of 110°, the unmodified line was practically absent, certainly less than 4 percent of the modified. This seems to prove that the Compton effect cannot be attributed to anything other than true scattering. This also favors the hypothesis, suggested by A. H. Compton, that the unmodified line occurs when the energy imparted to the electron during the process of scattering is insufficient to eject it from the atom.

IN connection with the study of the Compton effect in the scattered x-radiation it is important to measure the relative intensity of the modified and unmodified lines. Once such measurements have been made with some accuracy, they may throw some light upon the question of how the orbital electrons take part in the scattering effect.

METHOD AND APPARATUS

For the measurement of the intensity of the secondary radiation a spectroscopic method was employed. The arrangement of the apparatus was similar in general character to that employed by Compton[1] for measuring the spectrum of the secondary x-rays scattered from carbon and is diagrammatically shown in Fig. 1.

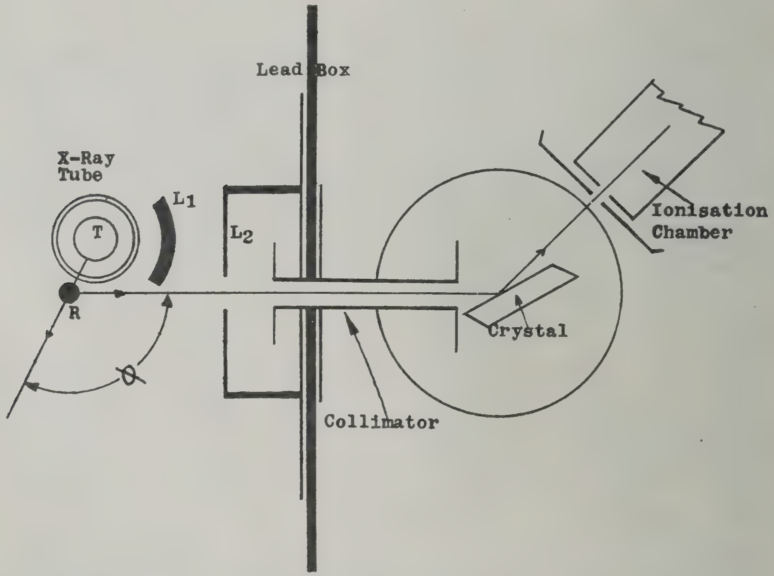

Fig. 1. Diagram of apparatus.

The primary x-rays from the target T of an x-ray tube fell upon the secondary radiator R, which was placed in line with the collimator. Lead screens, L_1 and L_2, disposed between the tube and the collimator, prevented stray radiation from leaving the lead box which contained the x-ray tube. The rays from the secondary radiator R, after passing through the collimator, struck the calcite crystal of the Bragg spectrometer, which reflected some of them into the ionization chamber. A sensitive Compton electrometer measured the ionization in the usual way.

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[1] A. H. Compton, Phys. Rev. **22**, 409 (1923).

The collimator, due to Soller,[2] was composed of a pile of sheets of lead foil separated by strips of lead foil. Two collimators, each with a length of about 17 cm, were employed in the present work. The x-ray tube, of small diameter, was of the type described by Compton.[1] For this work a current of 35 to 45 mil-amp. passed through the tube, coming from a generating plant consisting of transformers and kenotrons producing an intermittent direct current at about 65 peak kv. The primary voltage of the high tension transformer was supplied from the mains and was carefully controlled by an induction regulator so that the variation was kept within half a volt.

With these devices, and by using a large calcite crystal to reflect the broad beam from the collimator to the ionization chamber, it was possible to secure sufficient intensity without loss in resolving power. This seems to make a satisfactory apparatus for studying the intensity of the secondary radiation by the ionization method.

EXPERIMENTAL RESULTS

For the study of the energy distribution between the modified and the unmodified rays it was necessary to employ radiators of light elements in order to secure intensity sufficient for precise measurements. In the present experiments paraffin, wood, carbon (graphite), aluminium and sulfur were used as the scatterers. While the samples of paraffin, wood and carbon were in the form of a cylinder 1 cm in diameter, the aluminium and the sulfur were in the form of flat plates. In every case of the first four radiators the spectrum of molybdenum Kα rays was scattered at 60°, 75°, 90°, 105°, 120°, 135°, 150°, and 165° (in the case of aluminum no reliable result was obtained at 165°). Because of an accident to the x-ray tube, the experiments with sulfur were performed only at 75°, 90° and 105°.

One set of the experiments with paraffin as the secondary radiator is represented by Fig. 2, in which the curves represent the inoization current in arbitrary units as a function of the glancing angle of incidence of the rays on the calcite crystal. Curves similar to those in Fig. 2 were obtained for the experiments with wood, carbon, aluminium and sulfur as the radiators. Detailed tabulation of these results would be tedious and unnecessary. For measuring the spctra at 60°, 75° and 90° the width of the slits in the collimator was 0.2 mm, while for 150° and 165° the width of the slits was increased from 0.2 to 0.4 mm in order to secure greater intensity. For 105°, 120° and 135° both collimators were employed at convenience.

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[2] W. Soller, Phys. Rev. **23**, 272 (1924).

Two sets of experiments were performed with each of the five samples as the secondary radiator. From these measurements the distribution of energy between the modified and the unmodified lines was estimated. In view of the fact that the wave-length range investigated in the present work is small, we can assume to a close approximation that the energy in the different lines is proportional to the area under the ionization curves. This approximation is the more exact since the

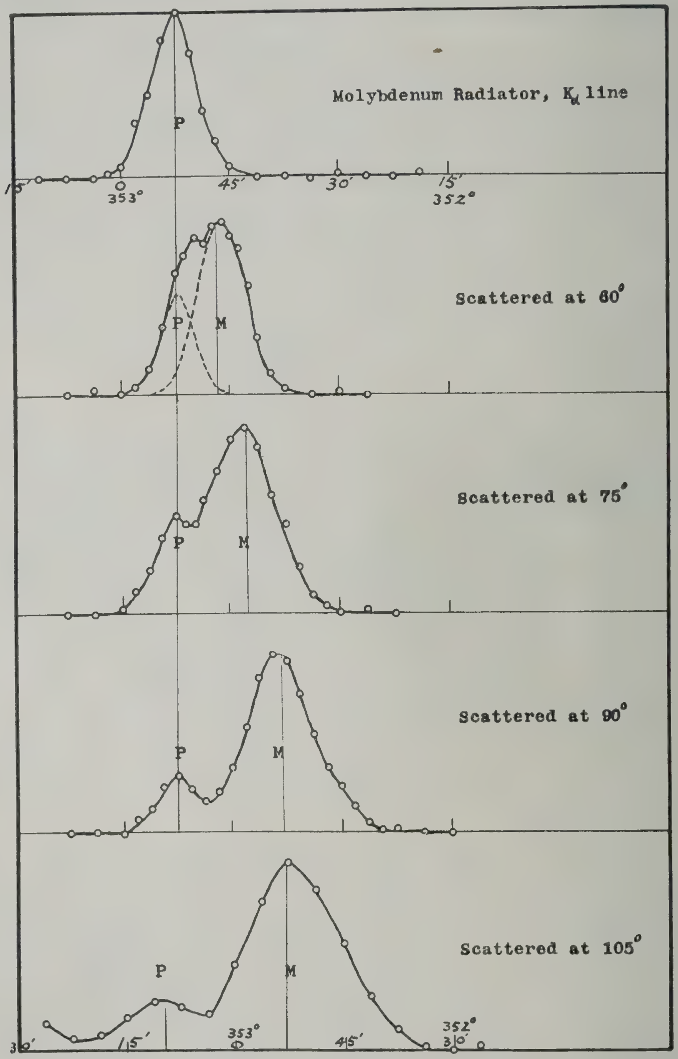

Fig. 2 (A). Intensity distribution of x-rays scattered from paraffin at various angles. *P* marks the position of the primary Mo K*α* line, *M* the position of the modified peak calculated from Compton's theory.

reflection coefficient of a calcite crystal is nearly independent of the wave-length, and since the ionization chamber was filled with ethyl bromide vapor and thus absorbed nearly all the x-rays of the wave-length studied. The relative energy of each spectrum was therefore obtained by integrating with a planimeter the area under the curve which represented the line.

Since the modified and unmodified lines were not distinctly separated from each other at 60°, the relative intensity was estimated by resolving the overlapping lines into two parts as shown in the second curve of Fig. 2(A). For measuring the spectra at 165°, the scatterer had to be placed so far away from the target of the tube (about 10 cm) that the measurement was made difficult by the reduction of the intensity of the incident radiation. Thus in the experiment on aluminium the 165° reading was repeated several times without success.

On integrating the area under the peak, attention should be called to the question of drawing the baseline of the ionization curve. It was found that when the collimator with narrow slits (0.2 mm) was employed, the general radiation under both the short wave-length side of the unmodified ray and the long wave-length side of the modified line was usually equally strong and so the line joining the readings of the general radiation is taken as the required baseline. However, when the collimator with wide slits (0.4 mm) was used, the general radiation under the former was always stronger than that under the latter. This was especially so if the scattering angle was large. Since the sensitivity of the electrometer was maintained constant by the use of a sputtered fiber, this effect is considered due to the presence of the modified beta peak. Thus the readings of the general radiation under the modified ray are taken to represent the height of the baseline of the modified and unmodified peaks. The curve representing the unmodified line is then completed to this adopted baseline in such a way that it has the same form as that of the fluorescent molybdenum Kα spectrum as shown in the second curve of Fig. 2(B).

In this connection we may mention the fact, pointed out by Allison and Duane,[3] that the intensity of the unmodified line relative to the general radiation is less in the scattered spectrum than when obtained direct from the target of the tube. This may perhaps be ascribed to (1) the presence of the modified beta peak in the secondary radiation as mentioned above and (2), as suggested by A. H. Compton, the presence of the second order of white radiation, which is excessively strong in the scattered rays due to the larger effective scattering volume in the radiator of the shorter wave-lengths. While the first effects depends on both the angle of scattering and the width of the slit, the second varies with the voltage put on the tube.

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[3] Allison and Duane, Phys. Rev. **26**, 300 (1925).

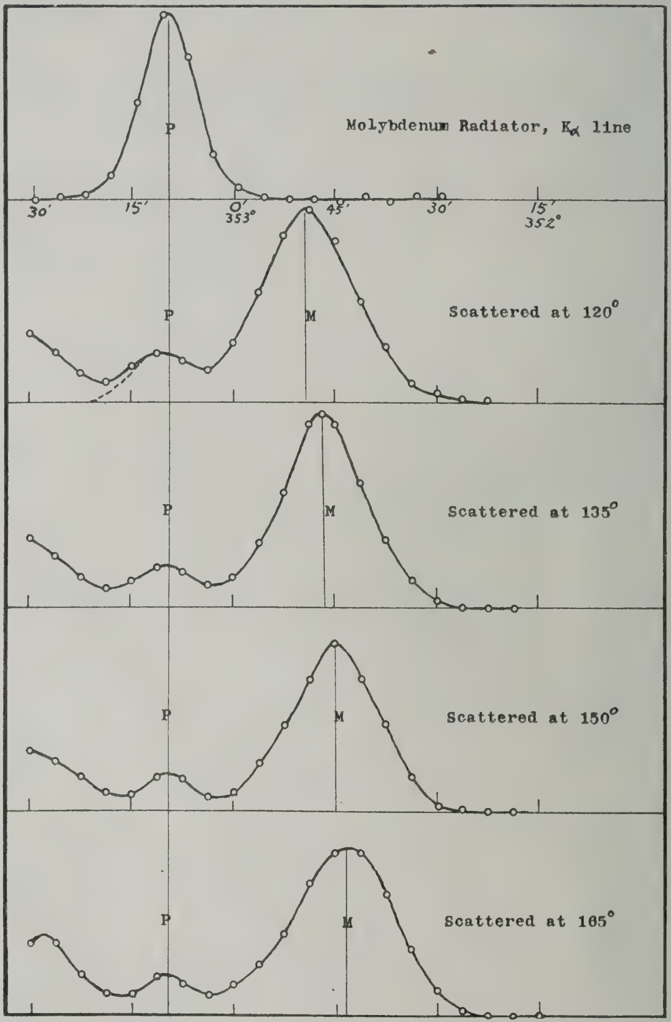

Fig. 2 (B). Intensity distribution of x-rays scattered from paraffin at various angles.

A special series of experiments was also performed by allowing primary rays of different intensities, produced by varying the current passing through the x-ray tube, to fall on a radiator at a definite distance from the target of the tube. It was found that the relative energy in the modified and the unmodified line is within the limit of experimental error independent of the intensity of the incident radiation.

The results of this measurement of the relative intensities are tabulated in Table 1, where ϕ represents the scattering angle, R the ratio of the energy expressed in arbitrary units in the modified ray to that in the unmodified, and s the width in mm of a single slit in the multiple-slit system.

TABLE I

Ratio of the energy in the modified line to that in the unmodified line for different radiators and various angles

	Wood		Paraffin		Carbon		Aluminium		Sulfur	
	s	*R*	*s*	*R*	*s*	*R*	*s*	*R*	*s*	*R*
60°	0.2	1.19	0.2	2.29	0.2	1.08	0.2	0.46	...	....
75°	0.2	1.85	0.2	3.10	0.2	1.31	0.2	0.74	0.2	0.25
90°	0.2	2.73	0.2	4.69	0.2	1.45	0.2	0.91	0.2	0.41
105°	0.2	3.21	0.4	5.16	0.2	1.82	0.4	1.23	0.2	0.67
120°	0.2	4.57	0.4	5.49	0.2	2.26	0.4	1.45	...	....
135°	0.4	5.38	0.4	6.52	0.2	3.42	0.4	2.11	...	....
150°	0.4	6.21	0.4	6.98	0.4	4.05	0.4	2.52	...	....
165°	0.4	7.00	0.4	7.47	0.4	4.86	...	....	...	....

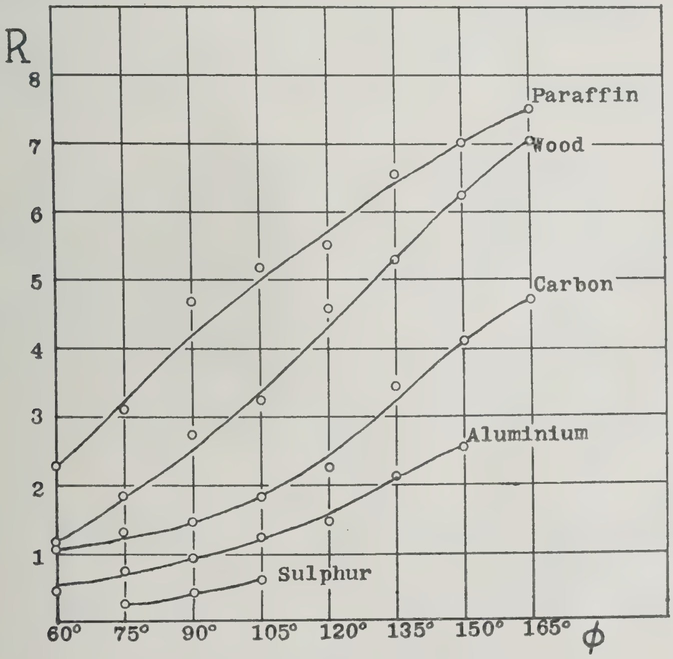

Fig. 3. $R-\phi$ curves for various radiators.

In Fig. 3 the intensity ratio R is plotted against the scattering angle ϕ. It appears that each set of data approximately fits a smooth curve, showing the variation of the intensity ratio as a function of the scattering angle. In all cases except for paraffin the experimental curve seems to be concave upward at small angles and convex upward at large ones. As the curve for paraffin is a little irregular, it may be noted that in this case the intensity of the unmodified ray is so small that the electrometer readings are relatively uncertain.

It is worthy of note that the unmodified line in the spectra scattered from graphite is more prominent than that in the spectra scattered from wood, and that in the spectra from paraffin the unmodified ray is particularly faint. Wood is composed of cargon, hydrogen and oxygen, whereas paraffin is a compound of carbon and hydrogen. This clearly indicates that the element hydrogen is most effective in scattering the modified line. In view of the faintness of the unmodified line in the spectra from paraffin it seems probable that the unmodified part of the scattered spectrum is entirely due to the carbon in it. Thus a spectrum scattered from hydrogen would have only the modified radiation. This consideration is supported by the study of the intensity of the secondary rays scattered from lithium, which will be described in the following section.

INTENSITY OF SECONDARY MoKα RAYS SCATTERED FROM LITHIUM

Unpublished results of experiments with lithium as the secondary radiator performed early in May, 1924, by A. H. Compton and the writer showed that, when the lithium sample was freshly prepared, the unmodified line was very faint, though it was undoubtedly present. The same effect has also been noted by B. Davis.[4] Recently Allison and Duane[3] have measured the scattered molybdenum Kα rays from lithium by keeping it from oxidizing with a coating of paraffin oil during the experiments. Their results still indicate the presence of a faint peak at the position of the unmodified line. As pointed out by these authors, their results may have been affected by the scattering from the carbon in the oil.

The writer recently performed a series of experiments by keeping the lithium radiator in a lead cell filled with hydrogen. Two mica windows, 0.005 mm thick, were provided on the lead cell, so that one of them allowed the primary x-rays to fall on the scatterer and the other permitted the secondary radiation from the radiator to pass into the collimator. Since the scattering from lead is negligible and since hydrogen is lighter than lithium, the present experiments were not affected by either of them. Special care was also taken to shield the wax cementing the mica windows.

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[4] B. Davis, Phys. Rev. **25**, 737 (1925).

The results of this measurement are shown in Fig. 4. Curve 1 represents one of the results of the experiments with the lithium sample cleaned in air, while curves 2 and 3 are two of the measurements obtained with the radiator carefully cleaned in an inverted glass jar filled with hydrogen. As far as they go, the results indicate that in the secondary x-rays scattered from metallic lithium the unmodified ray in the Compton effect disappears.

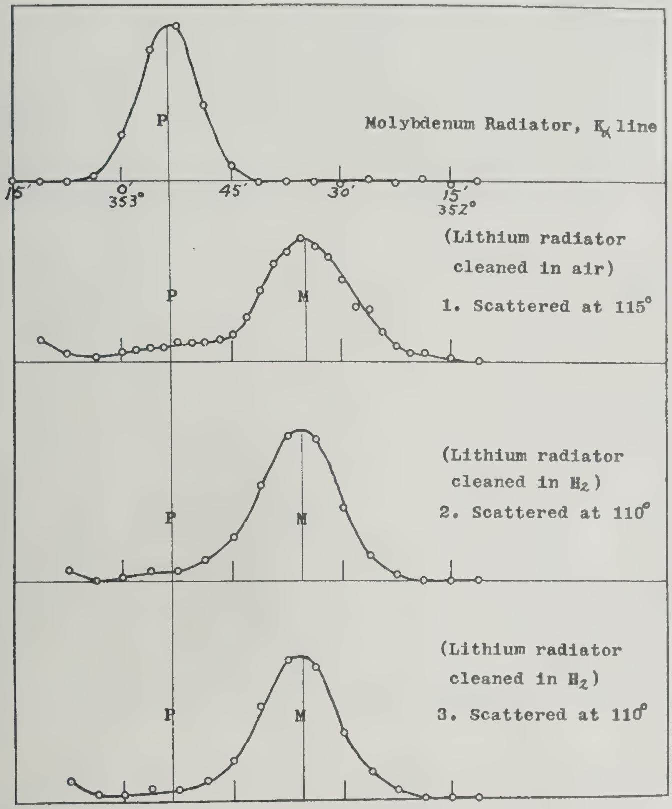

Fig. 4. Scattering from lithium. *P* marks the position of the primary Mo Kα line, *M* the position of the modified line calculated from Compton's theory.

Discussion of the Results

The discussion is conveniently divided into two parts: (1) The scattering from all the radiators except lithium and (2) the scattering from lithium.

(1) From results tabulated above it is seen that the energy ratio increases with the scattering angle in the way shown by the curves in Fig. 3. Since the conditions which determine whether an x-ray quantum shall be scattered according to the simple quantum law or in some other manner must also govern the distribution of the energy in the modified and unmodified rays, the present results thus point to the conclusion that the scattering angle should play in some way or other an important role in the determining factors.

A theoretical investigation of the question of the variation in the intensity ratio of the modified to the unmodified ray with angle of scattering for a given element and given incident wave-length has been recently published by Jauncey.[5] The theory requires an increase of the intensity of the modified relative to that of the unmodified line as the angle of scattering is increased. Unfortunately while the agreement between this theory and the present results is qualitative, it is not quantitative. Assuming a resolving power represented by 0.002A, Jauncey[5] gives for the ratio of intensity of modified ray relative to unmodified, 1.74 for carbon at 90° and 0.62 for sulfur at 90°, whilst the present experiments give for this ratio 1.45 for carbon at 90° and 0.42 for sulfur at 90° though the spectrometer arrangement in this work had a resolving power not greater than that corresponding to a wave-length width of 0.004A. This seems to indicate that Jauncey's theory overestimates the relative intensity of the modified and unmodified lines. However, it is of particular interest to note that the curve calculated according to Jauncey's theory to show the variation of the intensity ratio with the scattering angle is of the same general form as that of the curves in Fig. 3 obtained from experiments. This appears to point to the possibility of a further development of Jauncey's treatment.

Finally, it may be remarked that the present experiments also show that for a given angle of scattering the intensity of the modified ray relative to that of the unmodified line decreases as the atomic number of the scatterer increases, and that the width of the modified ray is greater than that permitted by Compton's simple equation. These are in accordance with the results of earlier work done in this field.

(2) From the result of the measurement of the intensity of the scattered radiation from lithium the following conclusions can be readily drawn.

First, it presents conclusive evidence that the Compton effect can not be attributed to anything other than true scattering, and therefore Barkla's idea[6] of differentiating these phenomena is difficult to defend.

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[5] G. E. M. Jauncey, Phys. Rev. **25**, 314 (1925) and Phys. Rev. **25**, 723 (1925).

Second, it favors Compton's first hypothesis[7] for accounting for the existence of the unmodified rays, that the binding energy of the electron is such that the energy imparted to the electron during the process of scattering is insufficient to eject it from the atom; but it is not quite consistent with his alternative hypothesis that the primary quantum is scattered by a group of electrons instead of a single one. It is also inconsistent with the possible explanation of the origin of the unmodified line that the primary quantum is scattered by the nucleus.

Third, it supports the consideration leading to the conclusion that the spectrum scattered from hydrogen would have no unmodified line.

In conclusion, the writer wishes to express his sincere thanks to Prof. A. H. Compton for his valuable suggestions and ever ready assistance during the course of this work.

Ryerson Physical Laboratory,
University of Chicago,
October 23, 1925.

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[6] C. G. Barkla, Nature, **114,** 753 (1924).

[7] A. H. Compton, Phil. Mag. **46,** 897 (1923).

PHYSICAL REVIEW FEBRUARY, 1926 VOL. 27

THE RELATIVE INTENSITIES OF REFLECTION OF X-RAYS FROM THE PRINCIPAL ATOMIC PLANES OF FLUORITE*

By D. A. MacInnes and Theodore Shedlovsky

Abstract

For these measurements, the usual Bragg apparatus was modified by adding a reference crystal illuminated through the same slit on a line slightly above the other, and a second ionization chamber and Bumstead electroscope. The integrated ionization as the crystal was turned by motor through a given line or range of wave-length was measured. Correction was made for the general radiation. Thus the relative intensities of the Pd α and β lines when reflected from three principal planes of fluorite were determined. The values fall into three groups for each line, each of which fall on a smooth curve when plotted as a function of the angle of reflection, the strongest group being due to Ca and F atoms acting together, a weaker group to Ca atoms alone, and the weakest group to Ca and F planes which are out of phase with each other. Simple quantitative relations between the intensities of these groups have not yet been found, evidently because an additional absorption by the crystal takes place, which varies in an unknown manner with the angle of reflection.

THE investigation to be described below was undertaken in the belief that the accurate determination of the intensities of reflection of x-rays from crystals will yield results which are nearly, if not quite, as important as the determination of the angles of reflection has proved to be. The final decision as to the structures of the more complicated crystals will undoubtedly depend upon exact quantitative determinations of relative intensities of the different orders of reflection from the various planes, in addition to the distances between atomic planes as obtained by measurements of angles. Many examples of the great value of intensity measurements in the determination of crystal structures are given in the work of W. H. and W. L. Bragg.[1] It is also certain that the intensities of reflection are intimately related to the arrangement of the electrons in the atoms.[2]

In the following pages a modification is described of the Bragg apparatus to adapt it to more accurate determinations of intensities. Results are also given of accurate measurements of relative intensities of several orders of reflection from the principal atomic planes of fluorite (calcium fluoride).

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* Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 176.

[1] W. H. and W. L. Bragg, "X Rays and Crystal Structure," Harcourt, Brace and Co.

[2] Bragg, James and Bosanquet, Phil. Mag. **41,** 309 (1921).

The Apparatus

The principle of the method for measuring the relative intensities is shown diagrammatically in Fig. 1. The x-rays from the target A pass through the slits S_1, S_2 and S_3 and strike the crystal under observation, C, from which the reflected rays pass to the ionization chamber E under which a Bumstead electroscope, which moves with the chamber, is swung. The crystal and chamber angles are read, in the usual manner, on the graduated scale V. In addition, x-rays which have passed through slits S_1 and S_2, but at a slight vertical angle to the rays which strike crystal C, are intercepted by the crystal C' and are reflected to the chamber E' which is connected with another Bumstead electroscope. The crystal C' and the chamber E' remain stationary. The electroscopes are calibrated by impressing successive potentials from a potentiometer between the leaves and the ground. The intensities of reflection are therefore found in terms of ratios of the potentials necessary to reproduce the observed deflections of the leaves of the electroscopes. A carborundum crystal C' is used for the reference, as it has a strong second order reflection at a large angle, so that the chamber E' can be placed in such a position that it does not interfere with the chamber E at small angles of reflection. The vapor of ethyl bromide is circulated by a hand operated pump through the chambers E and E' until the same partial pressure of vapor is present in both. It was found necessary to make both chambers gas tight.

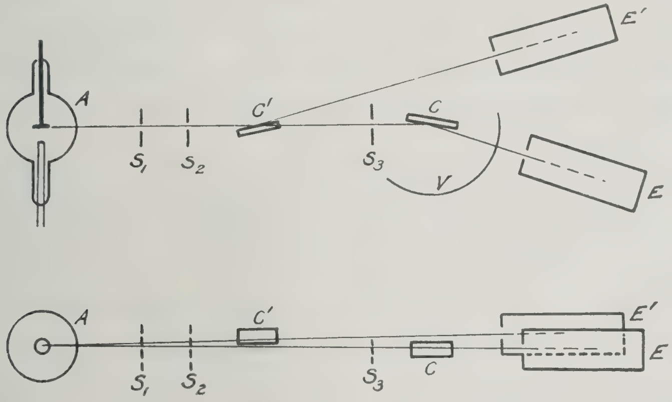

Fig. 1. Diagram of apparatus, showing the arrangement of crystals and ionization chambers.

This was not found possible with sulfur insulation of the wires leading to the electroscopes, and other insulators, e.g., sealing wax, soon became conducting in the presence of the ethyl bromide. However, a gas tight, perfectly insulating support was formed by using sulfur inside and sealing wax outside. This remained perfect for more than two years.

The Coolidge tube (A in the diagram) was very kindly presented to us by Dr. Coolidge of the General Electric Company. It is air cooled and supplied with a palladium target. It was found necessary to operate this tube continuously while making readings, and for several hours before, since otherwise the position of the target A changes, due to the expansion of the copper rod on which it is supported. The crystals are exposed to the rays simultaneously by moving a lead disk placed between the slits S_1 and S_2. The support of the crystal C' is arranged so that the crystal can be turned through a small angle. The slit S_2 consists of upper and lower halves which can be adjusted separately, making possible independent regulation of the width of the beams hitting crystals C and C'.

The ionization chambers E and E' are 8 in. long and 2 in. in diameter. They are fitted with thin mica windows behind the chamber slits, and with lead glass windows on the other end to aid in the optical adjustment of the crystals.

With this apparatus it is, of course, possible to determine the angles of reflection of the characteristic lines of the palladium spectrum. After locating the exact positions of these reflections from a particular crystal face, the proceedure for determining the relative intensities of the reflections for the α doublet and the β lines and for the various orders of reflection of those lines is as follows. The slit of the chamber E is given a width of 0.5 mm to 1 mm (1 mm = 40′) and adjusted so that the center of the slit is at the maximum of reflection for the line. Then the crystal C is rotated slowly (by means of an electric motor and a worm gear) through one degree, half of which lies on either side of the maximum of reflection in question. For a check measurement the crystal is then turned in the opposite direction through the same range. The time of rotation is regulated so that sufficient radiation has entered the ionization chambers to give large enough deflections of the electroscope leaves for an accurate measurement. For the weaker lines deflections from several rotations are allowed to accumulate in the electroscope connected with E, whereas the electroscope for E' is grounded before each reversal of the motion and a record is made of the sum of the successive deflections. In this way the intensities of the weaker lines are obtained with nearly as great accuracy as for the stronger ones. Besides the α and β characteristic radiations, this procedure involves reflection into the chamber of general radiation. A correction for this is made by obtaining a complete series of measurements on reflections at angles at which reflections of characteristic rays do not take place. It is then possible to draw smooth curves through the resulting points, and to find accurate values of the reflection of general radiation at angles at which characteristic reflection also takes place. These curves for general radiation indicate the structure of each crystal face in much the same manner as is done by the characteristic radiation. For instance, the (100) face of fluorite, which has a strong second and fourth order and almost no first and third order reflections, showed the same peculiarities in reflection of general radiation, maxima and minima of this reflection occurring on a smooth curve, at points corresponding to even and odd order reflections.

We have given considerable attention to the effect of the state of the crystal surface on the resulting reflection, and have found, as has been observed by Bragg and his associates[2] and by Dickinson,[3] that the most reproducible results are obtained from crystal surfaces that have been ground or roughened. In this work the (100), (110) and (111) faces were studied. Of these the first and last occur naturally and the second had to be ground artificially. Irregularities due to grinding were largely overcome by inverting the crystal after a series of measurements and repeating, and then averaging the result of the two sets of measurements. In this procedure we followed the suggestion of Bragg, James and Bosanquet.[2]

After determining the relative intensities for the different orders of reflection for the three principal planes it was necessary to bring these three sets of ratios to the same scale. This was done by observing the integrated effect in the electroscope of swinging each of the crystal faces through an angle large enough to include the α doublet and the β lines, and a certain amount of general radiation. The angle was chosen so as to include the same range of general radiation for each face. In this way the (200), (111) and (220) intensities were found to be in the ratios: 1.00, 2.47, 0.487.

In these measurements much use was made of the photographic method for locating reflections. The images on the films gave definite information as to whether the crystal was reflecting completely or only partially into the chamber slit. The orientation of the crystal with the purpose of excluding reflections from other planes than the one under measurement was also made possible by that method.

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[3] Dickinson and Goodhue, J. Am. Chem. Soc. **43,** 2046 (1921).

THE EXPERIMENTAL RESULTS

A summary of the results is given in Table I. All the intensities are given with reference to that of the (100) reflection which has arbitrarily been given the value 100.

TABLE I

The relative reflections of characteristic palladium rays from fluorite

Line	Angles		Relative intensities	
	α	β	α doublet	β
100	6°10′	5°26′	0.53	0.17
200	12°24′	10°55′	52.8	18.3
300	18°48′	16°30′	0.40	0.20
400	25°26′	22°15′	7.92	3.39
110	8°38′	7°37′	100.0	33.2
220	17°27′	15°22′	25.7	9.31
330	26°45′	32°25′	6.67	3.23
111	5°19′	4°42′	130.3	42.1
222	10°41′	9°25′	1.15	0.51
333	16° 9′	14°12′	16.2	5.73
444	21°46′	19° 6′	13.3	5.33

The ratios given in this table were determined as described above with the exception of the two values given for the (111) reflection. In that case the angle of reflection was so small that a separation of the α doublet from the β line for the purpose of measuring intensities was not possible, though the "peaks" were, of course, easily measured. To overcome this difficulty a measurement of the sum of the intensities of the α and β reflections was made, and an estimate (by methods to be described) was obtained of the ratio of the two, from which the results in the table were computed. The measurement of the sum of the intensities was carried out by widening the chamber slit and swinging the crystal through a larger angle than in the determinations of the intensity of a single reflection. The ratio of the α to the β reflection for this line was then estimated in two different ways. First a short extrapolation was made of a curve in which the ratios of the α to the β intensities of all the stronger reflections were plotted against the mean angle of reflection. From the resulting smooth curve to the mean angle of the (111) reflection gave the ratio 3.08. Secondly, it was found that for the more intense reflections a straight line was obtained, for both the α and the β series, when the intensities were plotted against the inverse sine of the angle of reflection. A short extension of these two lines to angles corresponding to the (111) reflections yielded values in the ratio of 3.09, which was adopted for the figures in the table.

DISCUSSION OF THE RESULTS

A plot of all the data in Table 1 is shown in Fig. 2 in which the square roots of the relative intensities are plotted against the reciprocal sines (cosecants) of the corresponding angles. For the α doublet reflections there are two curves connecting a series of points, and also two isolated points which are connected in the figure by dotted lines. For the β series there is a completely analogous series of lines and points. As plotted all the curves tend to converge toward a zero of intensity at a value of the abcissa of unity, i.e., an angle of 90°. Similar smooth curves connecting the intensity of reflection with a function of the angle of reflection have been found by Bragg and Bragg[1] and by Bragg, James and Bosanquet[2] for sodium chloride, and by W. H. Bragg[5] for diamond. The angles and intensities observed are in complete accord with the structure for fluorite proposed by Bragg and Bragg.[1] According to their analysis the arrangement of atoms in the various planes of the crystal is as shown in Fig. 3 in which the solid lines represent planes containing calcium atoms and the dotted lines planes of fluorine atoms. In the cubic (100) faces, planes of calcium atoms alternate

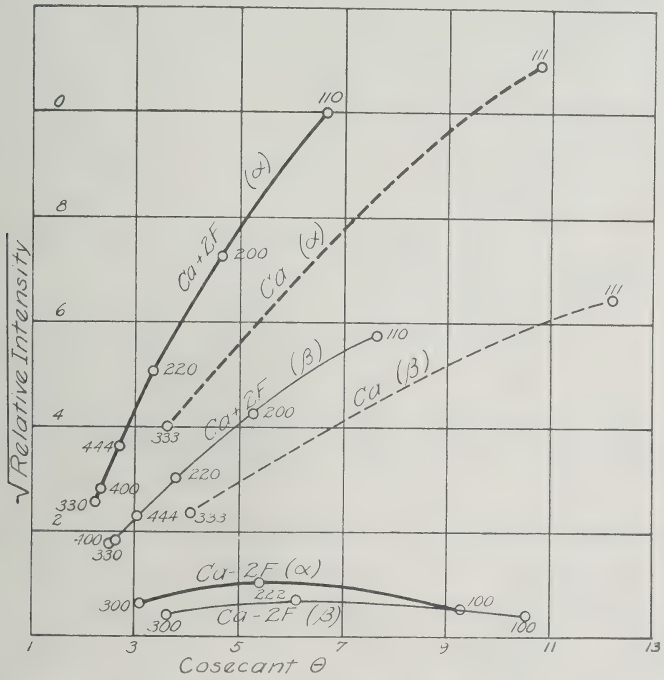

Fig. 2. Variation of the square root of the relative intensities with the cosecant of the corresponding angles.

with planes of fluorine atoms. This results in interference in the rays from alternate planes for odd orders of reflection, and reinforcement for even orders. Since the number of electrons in the calcium atom (20) is very close to that for the two fluorine atoms (18) the interference is nearly but not quite complete. (The numbers are the same, but interchanged, if the atoms are present as charged ions.) The planes of the prism (110) faces contain both calcium and fluorine atoms, and all the planes being alike the normal order of decrease of intensity for the various orders is observed. This decrease is 100, 25.7, 6.7 for the α doublet and 100, 28.0, 9.6 for the β reflections. The octahedral (111) planes are of somewhat more complicated character. Here in the distance d between the planes of calcium atoms, two planes of fluorine atoms are present, both spaced $d/4$ from the former planes. The result of this "quartered" arrangement is that the first order of reflection is due to the calcium planes only, since the rays from the two sets of fluorine planes are exactly out of phase with each other. On account of the small angle of reflection this intensity is higher than any of the others although due to scattering from only a portion of the atoms. In the second order (222) the reflection from the calcium planes is in opposition to the fluorine planes, and is thus similar to the (100) and (300) reflections. The third order (333) is similar to the (111), but for the (444) all the trains of waves are in phase and reinforce.

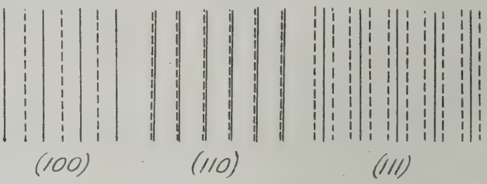

Fig. 3. The arrangement of the atoms in the various planes of the crystal of calcium fluoride according to W. H. and W. L. Bragg. The solid lines represent planes containing calcium atoms and the dotted lines planes containing fluorine atoms.

The reflections divide naturally into three groups: (a) those from mixed planes and those in which the waves from the calcium and fluorine planes are in phase (these form the curves marked Ca+2F in Fig. 2), (b) reflections from calcium alone, which are shown in the figure by points connected by dotted lines, and (c) reflections in which the fluorine planes are in opposite phase to the calcium planes, indicated by curves marked Ca-2F in the figure. It is interesting to note that the different orders of reflection from the octahedral (111) face contribute to all of the groups, and also that the Ca+2F curve contains points from the three planes measured. Bragg and Bragg did not report any of the reflections in group (c), but that for (100) has, however, been observed by Pealing.[4]

It would appear at first sight that it should be easy to compute values of intensity in any one of the groups (a), (b) and (c) from data given in the other two groups. This has not, however, been found to be the case. The reflections from calcium, for instance, which involve about half of the electrons have considerably more than half the intensity (at corresponding angles) of the reflections from planes involving all the electrons in the molecule. Quantitative agreement between the values in the different curves is, however, more nearly approached as the intensities decrease. A similar result, for diamond, has been observed by W. H. Bragg.[5] The phenomenon is undoubtedly due to an additional absorption, or extinction, of the x-rays at angles at which reflection takes place. A further discussion of this subject, and of the applicability of the Darwin-Compton equation for x-ray intensities to our results, will appear in another paper.

The authors wish to acknowledge the efficient assistance of Mr. Eric Townsend.

Research Laboratory of Physical Chemistry,
Massachusetts Institute of Technology,
November 25, 1925.

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[4] Pealing, Proc. Phys. Soc. London, **33**, 297 (1921).

[5] W. H. Bragg, Proc. Phys. Soc. London, **33**, 304 (1921).

K-SERIES EMISSION SPECTRA FOR THE ELEMENTS FROM TA(73) TO BI(83)

By B. R. Stephenson and J. M. Cork

Abstract

The specially designed water-cooled tube enabled currents of 8 milliamp. at 150 kv to be used. By connecting the same rheostat in the primaries of both high-tension and filament transformers, irregularity due to hot spots on the target was automatically smoothed out. An automatic electromagnetic cutout prevented excessive current when gas developed. With these arrangements, accurate measurements were made of the K-lines for all elements from Ta(73) to Bi(83) excepting Hg, the elements being placed in sheets or layers on the thin copper target. The $\sqrt{\nu/R}$ values plotted as a function of atomic number give practically straight smooth curves, as is to be expected. The differences in the ν/R values for the α and α' lines agree well with the corresponding values for $L\beta$ and $L\alpha'$. The corresponding wave-length differences are nearly constant and equal to 4.85.

UNTIL very recently the only two elements of the group from Ta(73) to Bi(83) for which the K-series emission wave-lengths had been measured were tungsten and platinum. Duane and Stenstrom,[1] Siegbahn,[2] Cork,[3] Lilienfeld and Seeman,[4] DeBroglie,[5] and Rogers[6] have measured one or both of these elements. Just recently Rechou[7] has published measurements on the elements from tantalum to uranium.

Apparatus

The spectrometer was of the type used by one of us in a previous investigation but was made larger. The distance between the second slit and the photographic plate was 75.593 cm. This gave a much larger separation of the lines on the plate. The plate holder was a rectangular frame machined out of one piece of solid brass and set optically perpendicular to the axis of the spectrometer. The photographic plate was held against the back face of the plate holder by three springs so that the emulsion side of the plate which faced the slit system was always the same distance from the second slit. X-rays were allowed to fall only on one side of the crystal at a time, thus giving all of the lines of the K series on one side of the plate simultaneously; the other half of the photographic plate being covered by a lead plate to prevent fogging during this time. The crystal was calcite and about 3 mm thick.

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[1] Duane and Stenstrom, Proc. Nat. Acad. **6,** 477 (1920).

[2] Siegbahn, Spectroscopy of X-rays, p. 104 (1925).

[3] J. M. Cork, Phys. Rev. **25,** 197 (1925).

[4] Lilienfeld and Seeman, Phys. Zeit. **19,** 269 (1918).

[5] DeBroglie, Comptes Rendus **169,** 134 (1919).

[6] Rogers, J. S., Roy. Soc. Victoria, Proc. **34,** 136.

[7] Rechou, M. G., Comptes Rendus **180,** 1107 (1925).

The x-ray tube was made with the target and filament removable at ground joints which were sealed with stopcock grease. The total tube length was about 18 inches, with the removable target 8 inches long and the ground stopper for the filament leads about 6 inches long. The target was of special design with two compartments so arranged that the part of the target which was in contact with the ground joint was always filled with the inflowing cold water while the heated water from the hot end of the target was carried by a tube through the center of the outer compartment and thus did not heat the joint. This enabled the use of tube currents as large as 6 to 8 milliamp. at 150 kv when elements with a high melting point were being used on the target. The filament was a spiral form of tungsten wire held in the filament container of a regular Coolidge tube which had been adapted to this apparatus. The lead wires were sealed in the outer end of the stopper to prevent puncturing such as often happened when the wires were sealed in at the inner end of the stopper. As both ends of the tube were different in potential from ground by half of the applied voltage, the leak through the target cooling water to ground was very large. With 55 feet of quarter-inch continuous glass tubing well insulated from ground the leak was from 6 to 7 milliamp. at the highest voltages.

The pumping system consisted of a two-stage mercury vapor pump with liquid air trap, backed by a rotary oil fore-pump. When the pumps and tube were working well, an x-ray vacuum could be obtained in about two or three hours. The time was shorter for the lower voltages.

The potential for the tube was obtained from a Victor Special 200 kv transformer and mechanical rectifier. The filament current was supplied by a Victor filament transformer. The voltage was regulated by means of an autotransformer and a rheostat in series with the primary of the high tension transformer.

Under ordinary conditions the tube current was unsteady, due to hot spots being produced on the target when some small bit of the powder became slightly detached from the target or when the sheet metals became slightly loosened and melted. This was overcome by using the same rheostat as part of the resistance of both the high tension primary and the primary to the filament transformer. Thus when the tube current tended to increase, the fall of potential over this common part of the resistance was increased and the filament current thereby diminished. This stabilizer held the current very steady as long as the voltage remained constant.

An electromagnet was placed with its exciting coil in parallel with the primary of the high tension transformer, and arranged to hold the primary circuit closed. When gas developed in the tube, as often happened, the tube current increased very much, causing the potential difference at the terminals of the high tension primary to fall; this allowed the electromagnet to open and thus break the circuit. The electromagnet was very quick acting and saved the tube as well as the rest of the apparatus from overheating. With these two devices it was possible to leave the apparatus for an indefinite period without fear of injury. A clock attached to the arm of the electromagnet was arranged to stop when the circuit was opened so that the time of exposure could be accurately determined. It was found that about 10 milliampere-hours at the proper voltage were necessary to give a strong exposure. The potential used varied from 120 kv for Ta to 156 kv for Bi.

All of the elements were obtained in as pure a form as possible. Tantalum, platinum, and gold were in sheets and were held on the face of the target. Platinum and gold were soldered to the copper face while tantalum, which could not be soldered, was wedged into a groove in the target. Osmium and irridium were powdered and rubbed onto the target. Two or three applications of the powder for each plate were sufficient. Thallium, lead and bismuth were flowed onto the target like solder. With all the elements, and especially with the last three, considerable difficulty was experienced because of the intense heat melting the element and sputtering the walls of the tube, causing it to puncture. It was not possible to get any of the elements in sufficiently good thermal contact with the target to avoid melting and sputtering. The face of the target was only about 2 mm thick and was made of copper to conduct the heat better and yet the high melting point metals became white hot at the focus. Since thallium, lead, and bismuth have such low melting points a very small tube current had to be used to avoid excessive sputtering. The tube was often taken down and cleaned, for it punctured easily if the walls became coated with sputtered metal.

MEASUREMENTS AND ACCURACY

This investigation was carried out in the second basement of the new Physics building where the temperature varied not more than 2°C at any time and usually not more than one degree. The plates and the length of the spectrometer were measured at the same temperature thereby eliminating any temperature effects. The length of the spectrometer was measured with a "Starrett" micrometer scale capable of measuring to 76.5 cm. This measurement was checked by making a rod with an adjustable end piece which could be set at the exact length between the slit and the plate and then measured on the same comparator as that used in measuring the plates. Grooves were filed out of the rod down to the center so that the rod could be measured in steps without having to change the focus of the telescope.

A distance of .25 mm on the plate corresponded to 1 x-unit and since the plates could be measured to 0.01 mm with a Gaertner comparator the measurements are certainly accurate to 0.1 x-unit. Four different crystals were used during the course of the investigation but no appreciable difference was observed in the values for the tungsten lines obtained.

RESULTS

Table I gives the values of the wave-lengths obtained. The values for tungsten obtained by one of us[3] previously, corrected for an error in the micrometer scale, as well as those of Duane and Stenstrom and Siegbahn are included for comparison. All of these values are corrected where necessary for any differences in the value of the crystal grating constant. The values obtained by Rogers[6] for platinum are also included.

TABLE I

Wave-length values in x-units of K series lines

Element	α'	α	β	γ	Investigators
73 Tantalum	219.73	214.88	189.91	184.52	Present
74 Tungsten	213.45	208.62	184.22	178.98	Present
	213.48	208.67	184.28	179.07	Duane and S.
	213.45	208.60	184.35	178.87	Cork
	213.52	208.85	184.36	179.40	Siegbahn
76 Osmium	201.31	196.45	173.61	168.75	Present
77 Iridium	195.50	190.65	168.50	163.76	Present
78 Platinum	190.04	185.23	163.70	158.87	Present
	189.54	185.11	164.37	159.55	Rogers
79 Gold	184.83	179.96	159.02	154.26	Present
81 Thallium	174.66	169.80	150.11	145.39	Present
82 Lead	170.04	165.16	146.06	141.25	Present
83 Bismuth	165.25	160.41	142.05	......	Present

Since the temperature of the laboratory remained practically constant at 22°C the value of the grating constant given by Siegbahn[2]

$\log 2d = 0.78235$ was used. No correction is made in the values of Table I for the effect of the refraction of the x-rays by the crystal. The magnitude of this correction is indicated by the following equation, $\lambda = 2d\ (1 - 0.000135) \sin \theta$. Thus the α line of tantalum 214.88 would become 214.85 x-units.

In Table II are given the frequency values ν/R, where ν is the reciprocal of the wave-length expressed in angstrom units and R is the Rydberg constant 109,737. These values are proportional to the energies emitted when the corresponding electron shifts occur.

TABLE II

ν/R values of K series lines

Element	α'	α	β	γ
73 Tantalum	4147.3	4240.8	4798.6	4938.6
74 Tungsten	4269.2	4368.2	4946.7	5092.4
76 Osmium	4526.7	4638.8	5249.0	5409.4
77 Iridium	4661.4	4779.8	5408.1	5564.7
78 Platinum	4795.9	4919.9	5566.8	5731.9
79 Gold	4930.2	5063.9	5730.5	5907.4
81 Thallium	5217.4	5366.8	6070.6	6267.9
82 Lead	5359.4	5517.8	6239.1	6451.3
83 Bismuth	5514.6	5680.9	6415.3	......

Table III gives the values of the square root of the frequency terms, $\sqrt{\nu/R}$. When these values are plotted with atomic number the curves shown in Fig. I are obtained. These points, shown by circles, fall very closely on smooth curves. The vaues obtained by Réchou, when they differ enough from our values to be indicated separately, are indicated by crosses. It is evident that some of his measurements show large deviations.

TABLE III

$\sqrt{\nu/R}$ values of K series lines

Element	α'	α	β	γ
73 Tantalum	64.40	65.12	69.27	70.28
74 Tungsten	65.34	66.09	70.33	71.36
76 Osmium	67.28	68.11	72.47	73.49
77 Iridium	68.28	69.14	73.54	74.62
78 Platinum	69.25	70.14	74.61	75.71
79 Gold	70.22	71.16	75.70	76.88
81 Thallium	72.23	73.26	77.91	79.17
82 Lead	73.21	74.28	78.99	80.32
83 Bismuth	74.26	75.37	80.10	.....

Table IV gives a comparison of the differences of the frequency values ν/R for the $K\alpha'$ and $K\alpha$ lines shown in column 2, and the results obtained by taking the frequency differences of the $L\alpha'$ and the $L\beta$ lines which represent the same energy differences, shown in column 3. The two columns agree fairly well. The values obtained by Réchou are also shown in column 4. In column 5 is given the wave-length difference ($\Delta\lambda$) between the $K\alpha'$ and $K\alpha$ lines. This wave-length difference for the relativity doublet is nearly constant for elements of large atomic number.

TABLE IV

Element	Doublet differences $\Delta(\nu/R)$ $K\alpha'-K\alpha$		$\Delta(\nu/R)$ $L\beta-L\alpha'$	$\Delta\lambda$ $K\alpha'-K\alpha$ (x-units)
	Our data	Rechoú		
73 Tantalum	93.5	96.8	92.7	4.85
74 Tungsten	99.0	100.6	98.5	4.83
76 Osmium	112.1	105.7	111.1	4.86
77 Iridium	118.4	113.0	118.6	4.85
78 Platinum	124.0	117.7	125.9	4.81
79 Gold	133.7	140.3	135.6	4.87
81 Thallium	149.4	172.3	150.5	4.86
82 Lead	158.4	158.9	160.0	4.88
83 Bismuth	166.3	164.7	169.7	4.84

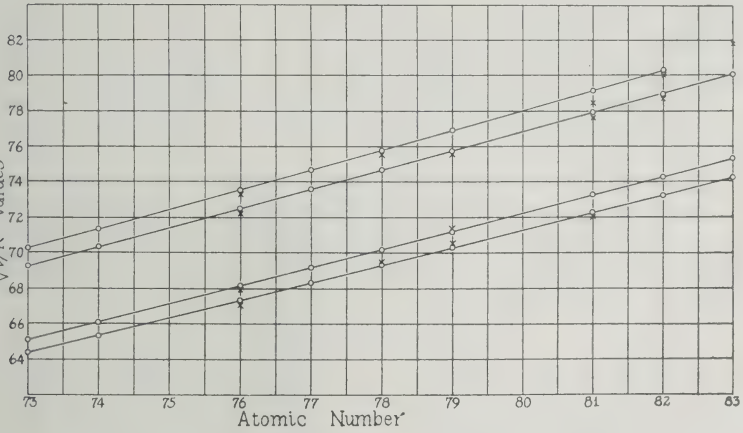

Fig. 1. $\sqrt{\nu/R}$ values as a function of atomic number.

The β line in every case appears much wider than the α' and the α lines, thereby indicating that it is complex. On some plates the components β and β' were sufficiently well defined to be separately measurable, but these are not recorded.

The x-ray tube was made of Pyrex glass which is supposed to be free from lead, but on every plate set for the measurement of short wave-lengths the lead K absorption edge appeared. This cut off completely the γ line of bismuth even though the α', α and β lines appeared very black.

PHYSICS LABORATORY,
UNIVERSITY OF MICHIGAN,
October 24, 1925.

STRIPPED OXYGEN, O_{VI}, THE PP′ GROUP IN O_V, AND NEW ALUMINUM LINES IN THE EXTREME ULTRA-VIOLET

By I. S. Bowen and R. A. Millikan

Abstract

Lines of stripped oxygen O_{VI} and of O_V.—The oxygen atom holds its last electrons so tenaciously that hitherto no lines assignable to stripped oxygen have been obtained. Using aluminum electrodes and high resolution, the "lithium doublet" of stripped oxygen has been definitely located at 1031.98, 1037.69A (see Plate I) the component of shorter wave-length being, as usual with this doublet, the more intense. The use of pure Al electrodes has also enabled the *pp′* group of O_V to be obtained in the fourth order, definitely resolved as a sextuplet (see Plate II) the ratio p_1p_2/p_2p_3 coming out 2.27, reasonably close to the value 2 called for by Lande's interval rule.

New aluminum lines between 1250 and 500A.—Fifteen new faint lines have been discovered and all definitely placed in their proper series, belonging to Al_{III} and Al_{II}.

Ionization potentials of stripped atoms.—Extrapolation from the known values for stripped atoms in the first and second rows of the periodic table, gives values for the $2s$ term which correspond to the following ionization potentials: for N_V 97.39; for O_{VI} 137.35; for F_{VII} 184.07; and for Cl_{VII} 113.73 volts. These are probably accurate to within 0.2 volt.

1. Stripped Oxygen

In preceding work we have been able to strip off completely the valence electrons from all of the elements contained in the first two rows of the periodic table[1, 2, 3] save only oxygen and fluorine. These two atoms hold the last of their valence electrons more tenaciously than do any of the others—the quantitative analysis follows later—and would therefore be expected to be the most difficult to reduce to the stripped condition.

In our earlier plates we sought for evidences of the stripped oxygen atom (O_{VI}) without finding any lines which could be unambiguously assigned to it. Since we have been using a very narrow slit and high resolution, some of our plates have revealed two faint but very definite lines which we can now obtain in both first and second order spectra and which, as is conclusively proved below, constitute the "lithium-doublet" of stripped oxygen.

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[1] Millikan and Bowen, Nature, **114**, p. 380 (1924).

[2] Bowen and Millikan, Phys. Rev. **24**, p. 209-222 (1924).

[3] Bowen and Millikan, Phys. Rev. **25**, p. 295-305 (1925).

These lines come out best when the electrodes used are pure aluminum, rather than salt-impregnated cores, for the latter tend to lower somewhat the vacua and especially the potentials to which the tips of the electrodes are raised before the spark occurs. It may be remembered that we have shown previously[4] that so-called "chemically pure aluminum" furnished primarily the oxygen spectra between 250A. and 1300A. The two new oxygen lines are shown in Plate I. Their measured wave-lengths are shown in Table I.

TABLE I

Lines of stripped oxygen O_{VI}

Intensity	λ I.A. Vac.	ν	$\Delta\nu$	Series designation
1	1031.98	96901.6	533.8	$2s-2p_1$
0	1037.69	96367.8		$2s-2p_2$

When the frequency ν and the frequency-separation $\Delta\nu$, corresponding to these two lines are subjected to the test of the regular and irregular doublet-law-progressions with atomic number, such as we have brought to light in preceding papers[2,5] there result Tables II and III, respectively. The perfect fitting of these two lines into both these tables removes all uncertainty as to the correctness of their identifica-

TABLE II

Regular L doublets, one-electron systems

$2p_2-2p_1$

Element	$\Delta\nu$	$\sqrt[4]{\Delta\nu/.365}$	s
Li_{I}	.338	.981	2.019
Be_{II}	6.61	2.063	1.937
B_{III}	34.4	3.116	1.884
C_{IV}	107.4	4.142	1.858
N_{V}	259.1	5.162	1.838
O_{VI}	533.8	6.184	1.816

TABLE III

Irregular L doublets

$2s-2p_2$

Element	$\Delta\nu$	Diff.	2nd Diff.
Li_{I}	14903.8		
		17023.8	
Be_{II}	31927.6		592.7
		16431.1	
B_{III}	48358.7		308.6
		16122.5	
C_{IV}	64481.2		148.6
		15973.9	
N_{V}	80455.1		61.2
		15912.7	
O_{VI}	96367.8		

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[4] Millikan and Bowen, Phys. Rev. **23,** p. 1-34 (1924).

[5] Bowen and Millikan, Phys. Rev. **26,** p. 310-318 (1925).

tion as the "lithium doublet" lines of stripped oxygen (O_{VI}). It will be noticed, also, from a glance at Plate I that these lines follow the rule which also holds for this lithium doublet that the component on the short wave-length side is the stronger.

2. IONIZING POTENTIALS OF STRIPPED ATOMS

The excitation of the O_{VI} atom from which these lines originate requires the highest energy of any optical series with which any one has thus far worked. The ionizing potentials of all the stripped atoms of the first row of the periodic table may be easily computed. Since the inmost p orbits of all the stripped atoms of the elements of this row are circular, for in this row they are $2p$ orbits, the progression of their terms and convergence frequencies with atomic number will follow closely the square law of the simple Bohr theory, i.e., the frequency of the $2p$ term of O_{VI} must be nearly 6^2 times that of lithium. More accurately, the study of the empirical progression of the value of

$$Z-\sigma=\sqrt{\nu n^2/R} \tag{1}$$

for the $2p_1$ term of the series of stripped atoms from Li through C yields, as previously pointed out by us,[1] the first four numbers of Table IV. The results of our extrapolation with the aid of these four values to corresponding values for N, O and F is shown in the last three numbers of the second column of Table IV. These numbers could scarcely be in error by as much as .005, which would correspond to not more than 0.2 volts in the resulting ionization potential. Computing from the foregoing formula the values of ν corresponding to these values of $Z-\sigma$ and then adding the frequency given in Table III of the $(2s-2p_1)$ line gives the frequencies of the $2s$ terms. These correspond to the ionization potentials shown in the fourth column of Table

TABLE IV

Ionization potentials of stripped atoms

Element	$2p_1$	Diff.	Ionization Potential	λ^{2s}
Li_I	1.02074			
		.02620		
Be_{II}	2.04694			
		.01707		
B_{III}	3.06401			
		.01056		
C_{IV}	4.07457			
		.00640		
N_V	5.08097		97.39	126.75
		.00381		
O_{VI}	6.08478		137.35	89.88
		.00224		
F_{VII}	7.08702		184.07	67.07

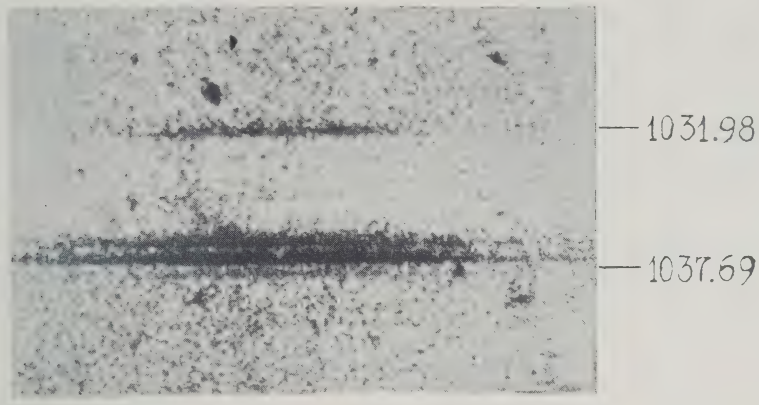

Plate I. The "lithium doublet" lines of stripped oxygen (O_{VI}).

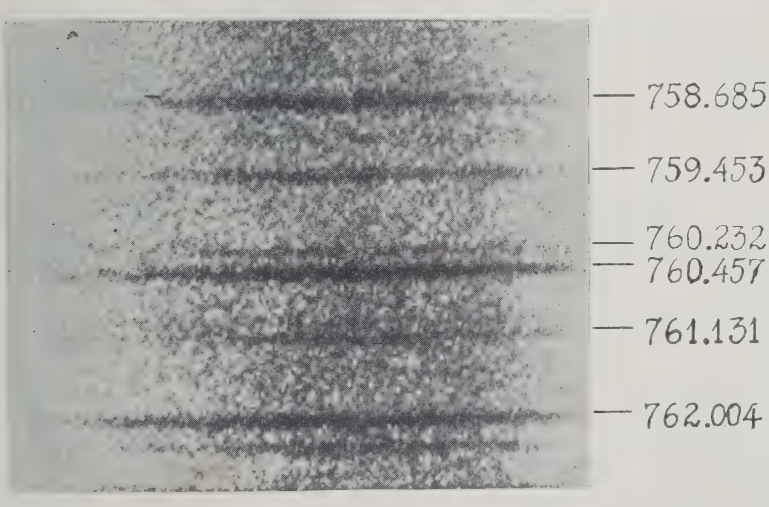

Plate II. The *pp′* group of stripped oxygen (O_V).

IV. The corresponding convergence wave-length of the principal series is given in the fifth column.

By a similar procedure the highest ionizing potential of any stripped atom of the elements in the second row of the periodic table, viz: that of chlorine (Cl VII), is found to be 113.73 volts. The corresponding value for sulfur is 87.6 volts, as we have previously shown.[3] It is obvious that the higher the value of this ionizing potential the more rapidly will the atom when once stripped begin to regain its valence electrons and hence the less the chance that it will be found emitting in the stripped state. This explains why the lines corresponding to stripped oxygen are more difficult to bring out than those corresponding to sulphur or even to chlorine.

3. The pp' Group in $\mathrm{O_V}$

The added sharpness and strength with which the $\mathrm{O_{VI}}$ and $\mathrm{O_V}$ lines come out when pure aluminum is used as electrode material has recently enabled us to obtain the pp' group in $\mathrm{O_V}$ in the fourth order spectrum where the resolution is so excellent that all of its six components are clearly separated, as is shown in Table V. This separation makes it possible to obtain, for the first time among the two valence electron atoms of the first row of the periodic table except Be (already known), the value of the ratio p_1p_2/p_2p_3. As may be seen from the numbers in Table V, the ratio comes out 2.27, in much closer agreement with the value 2 called for by Lande's interval-rule than is Be, which quite anomalously has the value[6] 3.57. Plate II shows the pp' group in $\mathrm{O_V}$ in the fourth order, with all of the six components definitely resolved and labelled.

TABLE V

pp' Group in two-valence electron oxygen $\mathrm{O_V}$

	p_1		p_2		p_3	
Int. :			(4)			
λ :			761.131			
ν :			131383.4			p'_3
$\Delta\nu$;			155.4			
Int.	(4)		(3)		(4)	
λ :	762.004		760.232		759.453	
ν :	131232.9	305.9	131538.8	134.9	131673.7	p'_2
$\Delta\nu$;	267.0		268.2			
Int. :	(5)		(4)			
λ ;	760.457		758.685			
ν ;	131499.9	307.1	131807.0			p'_1

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[6] Sommerfeld, Atombau und Spektrallinien, 4th ed., p. 661.

4. New Aluminum Lines in the Extreme Ultra-violet

In our former cataloguing of extreme ultra-violet lines we listed[4] but two lines between 1250A and 500A as certainly belonging to aluminum, viz., 859.9 and 695.9, and these of intensity 0 and 1, respectively. On our new plates we have been able to bring out these lines with greater intensity and resolution, and to cause fifteen other faint lines to appear, as shown in Table VI. All save four of these lines were predicted by Paschen,[7] his predicted values differing from our observed values only by a few hundredths angstroms, which is as close agreement as could be expected when we are working with lines so faint that they cannot be obtained in orders higher than the second.

Table VI

Series lines of aluminum, Al_{II} *and* Al_{III}

Intensity	λ I.A. Vac.	ν	Series designation	Stage of ionization
0	560.24	178494.9	$3s-5p$	III
3	695.82	143715.3	$3s-4p_1$	III
2	696.23	143630.7	$3s-4p_2$	III
0	725.74	137790.4	$3p_2-6s$	III
0	726.95	137561.0	$3p_1-6s$	III
3	854.98	116961.8	$3p_2-5s$	III
3	856.80	116713.4	$3p_1-5s$	III
1	892.00	112107.6	$3p_2-4d$	III
1	893.93	111865.6	$3p_1-4d$	III
0	1048.83	95344.3	$3p_2-5d$	II
0	1050.01	95237.2	$3p_1-5d$	II
0	1162.59	86014.8	$3d-6f$	III
1	1189.07	84099.3	$3p_3-4d$	II
2	1190.07	84028.7	$3p_2-4d$	II
2	1191.83	83904.6	$3p_1-4d$	II
0	1209.25	82695.9	$3p_3-5s$	II
1	1210.12	82636.4	$3p_2-5s$	II
1	1211.93	82513.0	$3p_1-5s$	II

Norman Bridge Laboratory of Physics,
California Institute of Technology,
Pasadena, California,
November 4, 1925.

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[7] Paschen, Ann. d. Physik, **71**, p. 142-161, 537-561 (1923).

PHYSICAL REVIEW FEBRUARY, 1926 VOL. 27

THE ABSORPTION SPECTRUM OF TIN VAPOR IN THE ULTRAVIOLET

By R. V. Zumstein

Abstract

Spectrum of tin.—(1) *Arc spectrum.* The spectrum of a 25 ampere arc was measured between 2170 and 1950A and 12 new lines observed. (2) *Absorption spectrum of tin vapor, 6000 to 2000A.* The tin was heated in a small carbon tube to about 1600°C and 53 absorption lines were observed, of which 38 are new. (3) *Frequency differences.* The results in general support the table of frequency differences given by McLennan, Young and McLay, lines from the normal state X_6 and X_5 showing strong absorption, those from X_4 medium absorption, those from X_2 only faint absorption and those from X_1 no absorption. A new table containing some changes and additions is given, using a different notation, which includes nearly all the arc lines. While the numerical relationships of the energy diagram are now well known, the nature of the terms involved has not yet been determined.

ALTHOUGH the number of lines in the tin arc spectrum is not large, the study of the spectrum from the series viewpoint has made very slow progress. A large percentage of the arc lines are readily reversed (especially with a current of 25 amperes) but their distribution is apparently irregular. One cannot by inspection recognize triplets or doublets. It frequently happens that the absorption spectrum of the vapor of an element furnishes a valuable clue to the relationships between the lines. Grotrian[1] has found four lines to be absorbed by tin vapor. McLennan, Young and McLay[2] have extended this number to 16.

The present experiments were undertaken using the methods that were employed in the study of manganese vapor.[3] Between 6000A and 2000A, 53 absorption lines were observed. If the absorption spectrum is photographed with the vapor at the highest temperature (about 1600°C), the intensities of the absorption lines fall quite naturally into three classes, very faint (f), medium (m) and the strongest absorption lines (S). One would expect that the strong absorption lines are due to atoms in the normal state while the very faint lines indicate atoms in excited states.

Table I contains the wave-lengths of all the known lines of the arc spectrum of tin below 6000A together with their frequencies. From

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[1] W. Grotrian, Zeits. f. Physik **18,** 169 (1923).

[2] McLennan, Young and McLay, Trans. Roy. Soc. Can. Sec. III, 57 (1924).

[3] Zumstein, Phys. Rev. **26,** 765 (1925).

6000 to 2190A Arnolds'[4] values of the wave-lengths are used. The intensities are as given by Kayser and Runge. Between 2190 and 1950A, the wave-lengths are my own values. The intensities are rough visual estimates of the spectrum of a 50 ampere arc. The maximum error of my measurements appears to be .1A above 2020A and .2A below 2020A. These values may be compared with the measurements of McLennan, Young and McLay[2] who first called attention to the important group of tin arc lines in this region. With a few exceptions, the agreement is very good. Two of their lines are resolved into doublets and 12 new lines are added to their list. Below 1950A the wave-lengths are those found by McLennan, Young and McLay as reversals of a tin arc in an

TABLE I

Tin arc spectrum

λ(I.A.)	ν(I.vac.)	Int.		Origin
		Arc	Abs.	
5631.69	17751.7	5	—	V
4524.740	22094.54	5	—	V
11.30	22160.4	2	—	—
4077.73	24516.5	1	—	—
3801.031	26301.21	4R	f	IV
3655.78	27345.5	3	—	V
3330.596	30016.04	6	*f*	IV
3262.338	30644.06	5R	*f*	IV
23.574	31012.54	1	—	—
18.690	31059.60	3	—	V
3175.039	31486.61	5R	*S*	III
41.823	31819.47	3	—	V
3067.76	32587.62	2	—	—
34.116	32948.96	6R	*S*	—
32.783	32963.45	3R	—	V
09.138	33222.46	6R	*S*	II
2913.542	34312.47	4R	—	V
2863.320	34914.29	6R	*S*	I
50.618	35069.84	4R	*f*	IV
39.985	35201.13	8R	*S*	III
13.582	35531.08	3R	*f*	IV
12.566	35544.28	3	—	V
2790.187	35829.35	2	—	—
89.323	35840.45	1	—	—
87.936	35858.26	4R	—	V
85.027	35896.15	3R	*f*	IV
79.814	35963.03	4R	*f*	IV
61.784	36197.82	4	—	—
06.504	36937.10	7R	*S*	II
2661.245	37565.23	4R	*S*	II
36.988	37910.76	3u	—	V
32.6	37974.		—	V
23.5	38105.		—	V
21.7	38132.		—	V
20.6	38148.		—	—
14.177	38241.55	1	—	—
2599.4	38459.		—	V
94.431	38532.59	4R	*f*	IV
71.598	38874.70	5R	*f*	IV

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[4] Arnolds, Zeits. f. wiss. Photographie **13**, 322 (1914).

TABLE I—continued

λ(I.A.)	ν(I.vac.)	Int.		Origin
		Arc	Abs.	
58.056	39080.47	4r	—	V
46.552	39257.00	5R	*S*	I
31.122	39496.31	4r	—	V
23.912	39609.13	3R	*f*	IV
10.9	39815.		—	—
2497.724	40024.39	2	—	V
96.768	40039.70	2	—	—
95.722	40056.50	5R	*f*	IV
91.71	40121.0	2r	—	V
83.389	40255.42	5R	*S*	III
55.250	40716.73	3	*f*	III
2433.473	41081.01	2	—	—
29.490	41148.41	6R	*S*	III
21.690	41280.93	6R	*f*	IV
08.143	41513.13	4R	*f*	IV
2380.742	41990.90	3R	*m*	II
68.217	42212.94	1	—	—
57.88	42398.0	1	—	IV
54.840	42452.73	6R	*S*	II
34.799	42817.09	5R	*S*	II
17.21	43142.1	6R	*f*	IV
2286.65	43718.5	4R	*m*	III
82.222	43803.32	3	—	IV
68.902	44060.53	6R	*S*	III
67.160	44094.37	4R	*f*	IV
51.12	44408.9	4R	*f*	IV
46.02	44509.7	6R	*S*	I
31.68	44795.3	4R	*m*	III
11.0	45214.	2R	—	IV
09.60	45242.9	6R	*m*	III
2199.29	45454.9	6R	*S*	II
94.42	45555.8	5R	*m*	III
71.21	46042.8	3R	—	IV
66.72	46137.4	1R	—	—
51.37	46467.3	3R	*f*	III
48.71	46524.8	3R	*m*	IV
48.44	46530.6	3R	*f*	II
47.81	46544.3	1R	—	IV
41.34	46684.9	2R	—	IV
40.65	46700.0	2R	*f*	III
23.61	47074.8	1R	—	IV
21.25	47126.9	2R	*f*	IV
18.51	47187.6	1R	—	IV
13.97	47289.4	3R	*S*	II
00.83	47585.1	4R	*m*	III
2098.77	47631.8	1R	—	IV
96.19	47690.4	4R	*f*	IV
94.20	47735.7	2R	*m*	III
93.77	47745.5	1R	—	—
92.41	47776.5	1R	—	IV
91.58	47795.4	3R	*S*	III
85.60	47933.4	1R	—	IV
84.19	47964.9	1R	—	IV
80.51	48049.7	2R	*f*	IV or III
74.75	48183.0	1R	—	—
72.86	48226.9	6R	*S*	I
68.47	48329.3	4R	*m*	III
63.95	48435.1	2R	*m*	II
61.42	48494.7	1R	*m*	IV
59.56	48538.5	1R	*f*	IV
2058.28	48569.0	2R	—	IV
54.05	48670.1	2R	—	IV
40.85	48983.4	3R	*m*	I

Table I—continued

λ(I.A.)	ν(I.vac.)	Int.		Origin
		Arc	Abs.	
40.53	48990.9	3R	*m*	III
28.56	49280.0	1R	—	IV
27.15	49314.3	2R	*f*	II
20.79	49469.4	1R	*f*	II
15.75	49593.3	2R	*f*	III
07.90	49787.2	2R		II
1994.30	50126.6	2R		I
92.67	50167.6	1R		—
91.14	50206.1	2R		III
83.39	50402.5	3R		III
70.75	50726.0	2R		II
59.60	51014.4	1R		I or II
51.54	51224.8	3R		III or I
47.6	51329.0	1R		II
41.81	51482.2	1		I or IV
32.32	51734.4	1R		III
24.50	51945.3	2		II
12.61	52268.1	1		III
λ(I.vac.)				
11.3	52320	R		III
08.8	52389	R		—
1899.63	52641.8	3		—
97.05	52713.4	1		I
91.1	52879	R		III
85.8	53028	R		I
82.7	53115	R		III
81.4	53152	R		III
73.3	53382	R		II
72.2	53413	R		—
71.1	53444	R		II
65.6	53602	R		II
63.1	53674	R		III
61.3	53726	R		III
60.3	53755	R		III
54.2	53932	R		II
52.0	53996	R		II
48.5	54098	R		—
37.4	54425	R		III
29.1	54672	R		III
23.1	54852	R		II
19.3	54966	R		III
15.6	55078	R		I
13.0	55157	R		I
08.8	55285	R		I
1804.6	55414	R		II
03.2	55457	R		II
1795.7	55688	R		I
92.0	55803	R		I
87.4	55947	R		—
80.4	56167	R		II
79.3	56202	R		II
78.0	56243	R		I
73.4	56389	R		I
72.8	56408	R		II
71.4	56452	R		—
66.8	56599	R		—
65.7	56635	R		—
64.8	56664	R		III
63.6	56702	R		II
61.7	56763	R		—
56.1	56944	R		—

atmosphere of hydrogen, and are a very valuable contribution to our knowledge of the tin arc spectrum. Those lines at which I have observed absorption by the vapor are indicated in column 4, Table I by the letters *f*, *m* or *S* which represent the magnitude of the observed absorption.

On the basis of their own experiments and the work of others (see their paper for complete references) McLennan, Young and McLay give a table of frequency differences. Sponer[5] has recently given a similar table. The faint arc lines reported by Sponer are also included in Table I. These two tables of frequency differences have been used to interpret the absorption experiments. Most of the lines of column X_6 (McLennan, etc. notation) show strong absorption supporting their opinion that these lines represent transitions to the normal state. Strong absorption is also observed for the lines which come from the X_5 state. This is not surprising as X_5 is an excited state differing in frequency from the normal state by only 1692 cm^{-1}. The absorption lines from the X_4 state ($X_6 - X_4 = 3428$ cm^{-1}) are in the medium class. From the X_2 state ($X_6 - X_2 = 8324$ cm^{-1}) only faint absorptions were observed and finally from X_1 ($X_6 - X_1 = 16873$ cm^{-1}) no absorptions were observed. In general, therefore, the intensities of the absorption lines support their table of frequency differences.

One naturally wonders if every tin arc line finds a place in this table or if there are more excited states close to the normal state. Several lines occupy two positions in their table. For example, 35544.3 (using frequency rather than wave-length) represents a transition to both the X_1 and X_3 states. The fact that no absorption was observed for this line shows clearly that the transition is to the X_1 state. 48676 is given as a transition to the normal state. It should therefore be absorbed rather strongly by the vapor. No trace of absorption was found. 41081.1 should be a medium absorption line but absorption was not observed. Proceeding in this manner, a new table of frequency differences has been made and is given in Table II. It is based primarily on the two tables already referred to and contains a few changes and several additions as suggested by the absorption experiments and the new arc lines observed. The X_3 state has been omitted as all the ultraviolet lines can be given other places in the table and also because the two red lines 16558.0 and 16845.3 were not observed reversed or absorbed. As regards notation, X_1 is used for the normal state, X_2 for the first excited state etc. From this list we get the last column of Table I. A line of origin IV is one where the transition is to the X_4 metastable state.

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[5] H. Sponer, Zeits. f. Physik **32**, 24 (1925).

Of the 53 absorption lines observed, 52 fit in Table II and in general with the approriate intensities. A glance at column 5, Table I, shows that the lines of the arc spectrum (below λ5600) which do not find a place in the frequency difference list are as a rule the faint emission

TABLE II

Frequency differences—tin arc

X_5V	X_4IV	X_3III	X_2II	X_1I (Normal state)
	8549.5	5185.5	1735.9	1692.
17751.7	26301.21	31486.61	33222.46	34914.29
	30016.04	35201.13	36937.10	
22094.54	30644.06		37565.23	39257.00
	35069.84	40255.42	41990.90	
	35531.08	40716.73	42452.73	
27345.5	35896.15		42817.09	44509.7
	35963.03	41148.41		
	38532.59	43718.5	45454.9	
	38874.70	44060.53		
31059.60	39609.13	44795.3	46530.6	48226.9
	40056.50	45252.9		
31819.47		45555.8	47289.4	48983.4
	41280.93	46467.3		
32963.45	41513.13	46700.0	48435.1	50126.6
	42398.0	47585.1	49314.3	(51014.4)
		47735.7	49469.4	
		47795.4		(51224.8)
34312.47		(48049.7)	49787.2	(51482.2)
	43142.1	48329.3		
	43803.32	48990.9	50726.0	
35544.28	44094.37		(51014.4)	52713.4
35858.26	44408.9	49593.3	51329	53028
		50206.1	51945.3	
	45214	50402.5		
	46042.2	(51224.8)		
37910.76			53382	55078
37974	46524.8		53444	
	46544.3	51234.4		55157
38105		51842		
38132	46684.9		53602	55285
38459			53932	
	47074.8	52268.1	53996	55688
	47126.9	52320		
	47187.6			55803
39080.47	47631.8			56243
	47690.4	52879		
	47776.5			56389
	47933.4	53115	54852	
	47964.9	53152		
39496.31	(48049.7)			
	48494.7	53674	55414?	
40024.39	48569.0	53755		
	48538.5	53726	55457?	
40121.0	48670.1			
		54425	56167	
	49280		56202	
		54672	56408	
		54966	56702	
	(51482.2)	56664		

Lines in parentheses occur in two places.

lines given only by Arnolds. It seems therefore very probable that some of these do not belong to the tin arc spectrum. Out of 40 lines observed by McLennan, Young and McLay in the Schumann region, only 9 are not classified. We have therefore considerable confidence in Table II and do not consider it probable that there are metastable states between X_1 and X_5. If the value of the X_1 term (59158) as given by McLennan, etc., is correct, then we can calculate the values of all the other terms. The problem of determining the nature of the individual terms is one of considerable difficulty and I have made practically no advance in that direction beyond a few general observations.

The vacant spaces in Table II are largely to be attributed to the selection principle of the inner quantum number. It is also certain that the 5 terms X_1, X_2, X_3, X_4 and X_5 do not at all belong to one system (for example quintet *d*) as there are terms which combine with all 5 and we would have a contradiction to the selection principle for inner quantum numbers. We should expect singlet, triplet, quintet, etc., systems for tin. If there are *p* terms among $X_1, \ldots \ldots X_5$ then by the interval rule the ratios of the separations would be 3/2 for quintets and 2/1 for triplets. We note that $(X_3-X_4)/(X_3-X_1)=3/2$. The very strong absorption line 3034.116 which could not be placed in Table II is one of the strongest absorption lines. It represents a transition to X_1, X_2 or X_3 and may be a combination between a quintet *d* term with inner quantum number 4 and *p* terms of the same system. This would explain the lack of other combinations with the particular term involved. Since we have two systems present it is to be expected that all lines which involve transitions to the X_4 term will be faint absorption lines if both terms are in the same system and may even not be observed as an absorption line if the terms belong to different systems and the dispersion of the spectroscope is not large enough. The lines from the X_1, X_2 and X_3 states while usually observed as strong absorption lines may be faint where we have an intercombination between two systems. In conclusion it may be said that the numerical relationship of the energy diagram for the tin arc spectrum are very well known; the nature of the terms involved, however, is practically unknown.

National Research Fellowship,
Physics Department,
University of Michigan,
October 31, 1925.

PHYSICAL REVIEW FEBRUARY, 1926 VOL. 27

SPACE CHARGE CURRENTS BETWEEN COAXIAL CYLINDERS IN THE PRESENCE OF A GAS

By W. H. McCurdy

Abstract

Approximate theoretical equation for space charge currents between coaxial cylinders with gas present.—Langmuir has derived an equation for the space charge limited current between coaxial cylindrical electrodes in high vacuum. In this paper Compton's equation for the terminal velocity of an ion suffering elastic collisions in an electric field, is applied to the case of space charge currents with gas present. Assuming the pressure sufficient so that the ions reach nearly the terminal velocity and neglecting the contribution of thermal agitation to the velocities of the ions, the following approximate equation is derived: $i=A\sqrt{lV^3/(aB)^3}$, where l is the mean free path, V is the voltage, a is the radius of the outer cylinder, B is a function of the ratio of the two radii (values are given in a table), and A is a constant depending on the charge and mass of the ions.

Introduction

It is well known that currents carried by ions between any pair of electrodes cannot exceed a definite value which depends on the form of the electrodes and the potential difference between them as well as on the charge and mass of the ions carrying the current. This limit is not in any way dependent on the supply of ions. Langmuir has found that for coaxial cylindrical electrodes in a high vacuum, this limit is given by the equation

$$i=\frac{2\sqrt{2}}{9}\sqrt{\frac{e}{M}}\frac{V^{3/2}}{r\beta^2} \tag{1}$$

where i is the current per unit length of the electrodes, e and M are the charge and mass of the ions, and β^2 is a function of the ratio of the radii of the outer and inner cylinders.

The present work is an attempt to derive an equation which will give the limiting currents which may be obtained when a gas is present in the space between the electrodes.

Derivation

Compton[1] has found that the terminal velocity which an electron, suffering elastic collisions, will attain in a gas is given by

$$V_t=\tfrac{1}{2}(\Omega+\sqrt{\Omega^2+E^2l^2\,M/1.134m}) \tag{2}$$

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[1] Compton, Phys. Rev. **22,** 334 (1923).

where V_t is the velocity in equivalent volts, and Ω is the velocity of thermal agitation, also in volts; E is the electric intensity and m and M the masses of the electrons and gas atoms respectively; l is the mean free path of the electrons.

Similar considerations yield for the terminal velocity of a positive ion, suffering elastic collision,[2]

$$U_t = \tfrac{1}{2}(\Omega + \sqrt{\Omega^2 + 4.61L^2E^2}) \tag{3}$$

where U_t is the terminal velocity, in equivalent volts, and L is the mean free path of the positive ion. The other symbols have the same significance as before.

Under certain conditions of pressure and electric intensity the velocity of thermal agitation becomes very small compared with the velocity due to the field. This is the case when the electric intensity becomes very large while at the same time the pressure is not so high as to make the mean free path extremely small. Then to a first approximation

$$V_t = \tfrac{1}{2}El\sqrt{M/1.134m} \tag{4}$$

and

$$U_t = \tfrac{1}{2}EL\sqrt{4.61} \tag{5}$$

If u is the velocity of advance of an ion and v_t its random velocity of agitation, it may easily be shown that

$$u = .75Eel/mv_t \tag{6}$$

from consideration of the distance of advance between collisions and of the velocity distribution of the ions.

Poisson's space charge equation for cylindrical coördinates reduces because of symmetry, to the form

$$\frac{d}{dr}\left(r\frac{dV}{dr}\right) = -4\pi\rho r = -2i/u \tag{7}$$

since $i = 2\pi r\rho u$, where i is the current per unit length of the electrodes, and ρ is the charge per unit volume of the space.

Substituting for u from (6)

$$\frac{d}{dr}\left(r\frac{dV}{dr}\right) = -\frac{8imv_t}{3eldV/dr} = -\frac{8i}{3}\sqrt{\frac{m}{el}}\sqrt[4]{\frac{M}{1.134m}}\,\frac{1}{\sqrt{dV/dr}} = A/\sqrt{dV/dr} \tag{8}$$

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[2] McCurdy, Phil. Mag. **48**, 899 (1924).

on substituting for V_t from (4) and putting

$$A=-\frac{8i}{3}\sqrt{\frac{m}{el}}\sqrt[4]{\frac{M}{1.134m}} \tag{9}$$

For simplicity, put

$$dV/dr=R$$

Integrating (8) we get

$$-\frac{2}{3}\log\left(A-R^{3/2}\right)=\log r+c\ . \tag{10}$$

For boundary conditions $r=a$ when $dV/dr=0$, where a is the radius of the outside cylinder which is the source of the ions.

Then, solving for c and reducing we get

$$R=A^{2/3}\frac{a}{r}\left(1-\left(\frac{r}{a}\right)^{3/2}\right)^{2/3} \tag{11}$$

Expanding the right side of (11) and substituting back for $R=dV/dr$ we get

$$dV=A^{2/3}\frac{adr}{r}\left\{1-\frac{2}{3}\left(\frac{r}{a}\right)^{3/2}-\frac{1}{9}\left(\frac{r}{a}\right)^{6/2}-\frac{4}{81}\left(\frac{r}{a}\right)^{9/2}----\right\} \tag{12}$$

Integrating (12)

$$V=A^{2/3}a\left\{\log r-\frac{4}{9}\left(\frac{r}{a}\right)^{3/2}-\frac{1}{27}\left(\frac{r}{a}\right)^{6/2}-\frac{8}{729}\left(\frac{r}{a}\right)^{9/2}----\right\} \tag{13}$$

The boundary conditions here are $r=a$, $V=0$ and $r=b$, $V=V_0$ where b is the radius of the inner cylinder. The first of these gives the value of the integration constant and substituting for $r=b$ we have (approx.)

$$V_0=A^{2/3}a\left\{\log\frac{b}{a}+\frac{359}{729}-\frac{4}{9}\left(\frac{b}{a}\right)^{3/2}\right\} \tag{14}$$

to terms in b/a only to the 3/2 power. For a closer approximation this may be carried to higher terms in b/a. If, now, we let

$$B=\left\{\log\frac{b}{a}+\frac{359}{729}-\frac{4}{9}\left(\frac{b}{a}\right)^{3/2}\right\} \tag{15}$$

then

$$V_0=A^{2/3}aB \tag{16}$$

Putting in the value of A, this reduces to an equation of the form

$$i=-\frac{3}{8}\left(\frac{el}{m}\sqrt{\frac{1.134m}{M}}\right)^{\frac{1}{2}}\frac{V_0^{3/2}}{(aB)^{3/2}} \tag{17}$$

The value of B depends only on the electrodes. The values of B and $B^{3/2}$ are given in Table I for values of the ratio of b/a from 0.500 to 0.005.

Eq. (17) applies to the cases of electron currents. The corresponding equation for positive ions is found to be

$$i = -\frac{3}{8}\left(\frac{eL}{2.15M}\right)^{\frac{1}{2}} \frac{V_0^{3/2}}{(aB)^{3/2}} \tag{18}$$

DISCUSSION

The general case of ionic currents between coaxial cylinders is very complicated and the present analysis is applicable only to a range of gas pressures and fields such that the contribution from thermal agitation to the velocities of the ions may be neglected in comparison with the velocities due to the field and such that the ion velocity has approximately the terminal value determined by momentum gain between collisions and loss at collisions. This latter condition implies numerous collisions in the space charge sheath. Most of the work of Langmuir

TABLE I

Values of (aB) *and* $(aB)^{3/2}$ *calculated for an electrode* b *of radius* 10^{-3} *cm.* A plot of this function on log paper produces a curve which is straight enough to make interpolation comparatively easy.

$(aB)^{3/2}$ may have the value given, multiplied by either $\pm\sqrt{-1}$. For electrons the factor must be considered as $+\sqrt{-1}$ while for + ions the value of $(V_0/aB)^{3/2}$ must be negative in order that the sign of the current may be correct. When V_0 is considered as positive, the observed current is negative. $\sqrt{-1}$ appears in both numerator and denominator of Eq. (18), since e is negative for electrons, and thus cancels. For positive ion currents e is positive but V_0 must be negative and aB is also negative so no imaginary occurs, but the negative sign must be taken as here the current is positive.

b/a	$-B$	$-(aB)$	$(-aB)^{3/2}$
.50	.358	$.0716(10)^{-1}$	$.608(10)^{-3}$
.45	.440	.0980	.975
.40	.536	.1340	1.550
.35	.658	.1870	2.56
.30	.784	.2615	3.98
.25	.949	.3790	7.36
.20	1.155	.576	13.80
.15	1.429	.951	29.40
.10	1.822	1.822	78.10
.09	1.930	2.145	99.50
.08	2.043	2.660	137.0
.07	2.166	3.10	173
.06	2.323	3.88	242
.05	2.498	4.98	355
.04	2.728	6.80	563
.03	3.013	10.05	1002
.02	3.418	17.10	1308
.01	4.108	41.08	8350
.005	4.828	96.60	29700

and Mott-Smith with exploring electrodes has been performed under conditions in which the use of Eq. (1) is justified. In some recent work at Princeton on the low voltage tube discharge, however, conditions were more nearly those postulated in the present analysis, which may be considered as the limiting case opposite to that treated by Langmuir.

An exact examination of the pressure and field conditions under which the present analysis may be expected to hold is extremely difficult. Rigorously it would hold only at infinite pressures and field strengths. This being the ideal condition, we wish to find at what pressures the desired conditions are approximately satisfied. In order to make this possible Table II has been prepared which gives the distances in which the ions attain a given fraction of their terminal velocity. If the calculation shows that the distance in which the ions have attained say 0.9 of their terminal velocity is small compared to the distance between the electrodes, we may be sure that the equations will give at least approximate results. This appears to be the only method of determining the conditions of applicability of the above equations.

TABLE II

The distance in which a given fraction of the terminal energy is attained by the ions in the field. Ψ is the fraction of the terminal velocity considered $d_{\bar{H}e}$, $d_{\bar{H}}$, $d_{\bar{H}g}$, are the distances in which the electrons attain this fraction of their terminal velocity. $d_{He}{}^+$ $d_H{}^+$, and $d_{Hg}{}^+$ are the corresponding distances for the positive ions of the gases indicated by the subscripts. p is the pressure of the gas in mm.

p (mm)	Ψ	$\overset{-}{d}_{He}$ (cm)	$\overset{-}{d}_{H}$ (cm)	$\overset{-}{d}_{Hg}$ (cm)	$\overset{+}{d}_{He}$ (cm)	$\overset{+}{d}_{H}$ (cm)	$\overset{+}{d}_{Hg}$ (cm)
1.0	.5	2.90	1.30	1.96	3.36×10^{-2}	1.76×10^{-2}	2.83×10^{-3}
2.0		1.45	.655	1.05	1.68	.88	1.41
3.0		.965	.430	.65	1.12	.58	.94
5.0		.573	.262	.392	.67	.35	.56
10.0		.290	.131	.196	.34	.18	.28
100.0		.029	.013	.0196	.034	.018	.028
1.0	.7	4.55	2.06	3.33	5.27	2.76	4.43
2.0		2.27	1.03	1.66	2.63	1.38	2.22
3.0		1.52	.68	1.11	1.76	.92	1.47
5.0		.91	.41	.66	1.05	.55	.89
10.0		.46	.21	.33	.527	.276	.443
100.0		.046	.021	.033	.053	.028	.044
1.0	.9	7.75	3.50	5.65	9.0	4.70	7.55
2.0		3.87	1.75	2.83	4.5	2.35	3.77
3.0		2.58	1.17	1.88	3.0	1.57	2.52
5.0		1.55	.70	1.13	1.8	.94	1.51
10.0		.78	.35	.57	.90	.47	.76
100.0		.078	.035	.057	.09	.047	.076

The evaluation of the constant of integration in Eq. (10) may seem to be incorrect; for since it is assumed that the velocity of the ions is proportional to the square root of the electric intensity, on substitution of a zero value for this at the outside electrode, we assume a zero value for the initial velocity of the ions, and thus the current must be zero, which is impossible. Since, however, the ions must have a velocity of thermal agitation they will diffuse into the space inside the outer electrode and there be caught by the electric field, while at the same time the velocity of agitation may be so small that it soon becomes insignificant in comparison with the velocity they obtain from the electric field. This means, of course, that the analysis cannot apply rigorously at the outer electrode. The effect of initial velocities on the motion of the ions in such cases as this has been recently considered by Langmuir and Mott-Smith.[3] Consideration of the initial velocities in the present analysis, owing to the limited range over which it is applicable, appears unnecessary. The general conclusion is that Eq. (18) may be used as an approximation provided collisions are sufficiently numerous in the gas between the electrodes to give the ions their terminal speeds quickly.

Though this derivation cannot be considered as rigorous and general, still it seems to give an advance in the direction of determining the effect of collisions on currents between cylindrical electrodes limited by space charge.

Palmer Physical Laboratory,
Princeton, N. J.
October 5, 1925.

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[3] Langmuir and Mott-Smith, G. E. Rev. **27**, pp. 449, 538, 616, 762 and 810 (1924).

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LOW VOLTAGE DISCHARGES IN HELIUM

By W. H. McCurdy and P. Dalton

Abstract

Discharge through helium, .01 to 2.9 mm pressure.—A hot filament cathode and disk anode were mounted in a glass frame 10 to 12 cm apart, the frame being so arranged that it could be moved magnetically inside a glass tube of diameter about 4 cm, with reference to a fixed exploring electrode. Measurements of *potential distribution and of mean energy and concentration of electrons* were made at three pressures, .095, 0.5 and 2.9 mm. Although precautions were taken to secure pure He, striations were obtained because of a trace of neon. The results are similar to those obtained by Bramley for hydrogen.[1] The mean electron energy decreases to a minimum beyond the negative glow, then rises to a maximum beyond the face of the first striation. The electron concentration falls from a maximum in the negative glow to a minimum near the cathode side of the first striation; within the limits of accuracy of the work, it increases in a given region of the discharge with an increase of pressure and is proportional to the current density of the discharge at a given pressure. Calculations of the *positive ion concentrations* by Langmuir's formula and also by one developed by McCurdy, give results which seem to be equal to the electron concentrations, but as both methods are merely approximations, this result is not very reliable.

Introduction

An investigation of the striated discharge in mercury vapor was reported by one of us,[2] but it was found that conditions were satisfactory for only approximate results. It was decided therefore to use helium instead of mercury vapor in order to secure more stable conditions without loss in the advantages to be derived from the use of a monatomic gas. It was found that helium served very well for the purpose of the work.

In the work referred to above the three following equations were used and the derivation of them indicated. Reference to the previous work may be made to secure information concerning these.

$$I=Ne\left(\frac{e\overline{V}}{3\pi m}\right)^{\frac{1}{2}}\epsilon^{-3V/2\overline{V}} \tag{1}$$

$$\overline{V}_{-}=\frac{3}{2\tan\theta} \tag{2}$$

$$I_0=Ne\left(\frac{e\overline{V}}{3\pi m}\right)^{\frac{1}{2}} \tag{3}$$

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[1] Bramley, Phys. Rev. **26,** (Dec. 1925).

[2] McCurdy, Phil. Mag. **48,** pp. 898-917 (1924).

In these I is the current per unit area of the exploring electrode and I_0 is the same when the exploring electrode is at the potential of the surrounding gas; V is the negative potential of the electrode with respect to the surrounding gas, and $\overline{V}_-$ the average velocity of the ions in equivalent volts; N the number of ions per cc of gas; $\tan\ \theta$ is $d(\log_e I)/dV$ of the $\log_e I$ *vs* V curves.

These equations permit the determination of the potential at any point in the field and of the concentration and average energy of the electrons, as indicated in the previous work.

In order to study positive ions, we must use a different method. Following Langmuir's[3] theory of space charge sheaths we are able, on making certain assumptions, to determine concentrations of positive ions. If the mean free path of the positive ion is large compared with the thickness of the space charge sheath, we may use Langmuir's[4] space charge equation,

$$i=\frac{2\sqrt{2}}{9}\sqrt{\frac{e}{m}}\ \frac{V^{3/2}}{r\beta^2}$$

where i is the current per unit length of the electrode and V the potential difference between the outside of the sheath and the exploring electrode, and thus determine the ratio of the radii of the outside of the sheath and the exploring electrode. Thus we have a method of calculating the radius of the sheath or the effective collecting area of the exploring electrode for positive ions.

When the ions make numerous collisions while traversing the space charge sheath, the above equation cannot be expected to hold. As this was the case in the most of the present work, an equation was used, which was developed to satisfy such conditions.[5] This equation evaluated for helium positive ions, is

$$i=3.14\times 10^{-7}\sqrt{L}\ \frac{V^{3/2}}{(aB)^{3/2}}$$

where i is the current per unit length of the electrode, L the mean free path of the positive ions and (aB) a function of the ratio of the radii of the sheath and exploring electrode. Both methods have been used in making the calculations and both results are given. Examination of the tables will show that, since in most cases the sheath thickness is large compared to the mean free path of the ions, the results obtained by use of the latter equation should be more reliable.

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[3] Langmuir, G. E. Rev. **26**, 731 (1923).

[4] Langmuir and K. Blodgett, Phys. Rev. **22**, 347 (1923).

[5] McCurdy, preceding paper in this issue.

In order to calculate the concentration of positive ions at any point in the discharge, we may now use Eq. (3) with appropriate values substituted for the charge and mass of the positive ions involved. This, of course, assumes a Maxwellian velocity distribution, which would be expected to correspond to the actual distribution, at least approximately. A more questionable factor is introduced in determining the average energy of the positive ions. In cases of weak electric fields, it is assumed that the velocity was that of thermal agitation of the gas molecules at the temperature of the gas, which was assumed to be 100°C. For cases of greater field strength, the terminal energy was calculated from the equation derived by one of us for positive ions.[6]

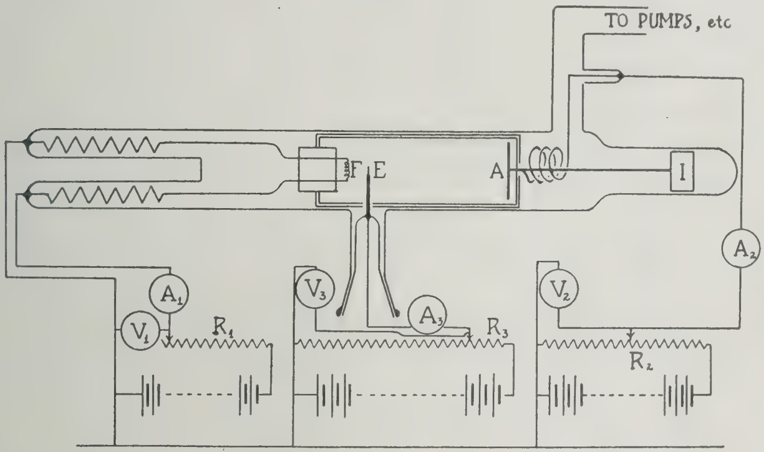

Fig. 1. F is the hot tungsten filament cathode, A is the anode and E the exploring electrode. $A_1 A_2 A_3$ are ammeters in different circuits and $V_1 V_2 V_3$ the corresponding voltmeters, R_1 R_2 R_3 are resistances or resistance potentiometers.

APPARATUS AND PROCEDURE

The experimental arrangement is shown in Fig. 1. The method used was that first developed by Langmuir[7] and used by him in a study of the discharge in mercury vapor. The anode and cathode were mounted in a light glass frame which could be fitted inside a glass tube about 4 cm in diameter. The distance between anode and cathode could easily be varied and the distances used ranged from 10 to 12 cm. The whole could be moved inside the discharge tube by means of an electromagnet and the iron cylinder I, thus making it possible to explore any desired part of the discharge by means of the fixed electrode. The electrical arrangements need no explanation.

[6] McCurdy, Phil. Mag. **48**, p. 898 (1924).

[7] Langmuir, G. E. Rev. **26**, 731 (1923).

The helium was purified, before being introduced into the experimental tube, by passing it over a mixture of copper and copper oxide heated to a dull red heat, then through cocoanut charcoal immersed in liquid air. Mercury vapor and stop-cock grease were kept from the system by means of liquid air traps into one of which some gold foil was introduced as an additional precaution against mercury vapor. The tube was carefully baked out before use by heating to about 350°C with good vacuum.

In perfectly pure monatomic gases the positive column is uniform. In spite of the above precautions, a trace of a striation was found at the cathode side of the positive column. This was assumed to be due to a trace of neon present in the helium, which could not be removed by the purification process employed. Spectroscopic evidence for this was found in a separate experiment, in which even more care was taken to remove all traces of impurity from the helium. The system, which included the purifying traps and discharge tube, could be cut off from the evacuation system by means of a mercury cut-off and was protected by liquid air traps. The whole was baked out to a temperature of 500°C under high vacuum and the copper-copper oxide mixture heated to a bright red heat. The metal anode was heated by means of an induction furnace until there was no glow produced by the furnace when the anode was at a very bright heat. The helium was then introduced after preliminary purification and the discharge started, which should cause the helium to flow through the hot copper-copper oxide mixture and through the charcoal in liquid air. Even after continued operation it was found that a trace of a striation still remained at the cathode end of the positive column. The only impurity that could be found spectroscopically was neon which showed very faintly. Thus it seems logical to assume that the neon was the cause of the striation observed. It may also be noted that this agrees with the theory advanced to explain striations in the positive column of the discharge,[8] since several of the critical potentials of neon, including the ionizing potential, are below the lowest radiating potential of helium.

RESULTS

Tables of the average energy of the electrons and concentrations of the electrons and positive ions under different conditions are shown in Tables I, II, III and IV in which the symbols have the following significance: $\overline{V}$ is the average energy of the electrons, N_- is the concentration and I_- the electron current per unit area of the exploring electrode; I_+ is the positive ion current per unit length of the exploring electrode, a_1 and a_2 are the radii of the outside of the sheath as calculated by Langmuir's and the author's equation respectively, N_1^+ and N_2^+ are the positive ion concentrations as calculated from the corresponding radii.

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[8] Compton, Turner and McCurdy, Phys. Rev. **24**, 597-615 (1924) also McCurdy, loc. cit.[2]

TABLE I

Results for helium at 2.9 mm pressure. Length of the discharge 11.6 cm. $\overline{V}_+$ assumed to be .049 volts in values marked*, otherwise $\overline{V}_+$ was calculated to be .110 volts. Tube current 90 m.amps. D is the distance from the anode.

D (cm)	I_- ($\times 10^2$)	$\overline{V}_-$ (volts)	N_- ($\times 10^{-9}$)	I_+ ($\times 10^3$)	a_1 ($\times 10^2$)	a_2 ($\times 10^2$)	N_1^+ ($\times 10^{-9}$)	N_2^+ ($\times 10^{-9}$)
Cathode								
11.35	252.	3.6	293.	1.75	1.57	2.11	*312.	*232.
11.0	197.	2.02	336.	1.12	1.86	2.56	*168.	*122.
10.5	79.	2.02	123.	.526	2.20	3.70	*57.	*40.0
10.0	27.8	2.22	42.	.253	3.0	5.25	*23.6	*13.5
9.0	5.91	2.46	16.5	.098	4.8	9.90	*5.7	*2.17
7.5	3.95	6.55	7.4	.112	4.9	10.6	4.27	2.02
1st Striation								
6.9	3.15	6.9	5.3	.161	4.6	10.1	6.55	2.9
6.3	3.15	8.0	4.5	.234	4.25	8.5	10.3	5.15
5.1	3.55	6.9	6.4	.365	3.68	7.05	18.5	9.60
2nd Striation								
4.4	3.79	8.35	12.2	.356	3.82	7.52	17.4	8.80
3.7	.52	6.0	9.3	.263	4.62	9.35	10.6	5.27
Anode								

TABLE II

Results for helium at .5 mm pressure. Length of the discharge 12.0 cm. $\overline{V}_+$ assumed to be .049 volts in values marked*, otherwise $\overline{V}_+$ was calculated to be .430 volts. Tube current 50 m.amps. D is the distance from the anode.

D (cm)	I_- ($\times 10$)	$\overline{V}_-$ (volts)	N_- ($\times 10^{-9}$)	I_+ ($\times 10^3$)	a_1 ($\times 10^2$)	a_2 ($\times 10^2$)	N_1^+ ($\times 10^{-9}$)	N_2^+ ($\times 10^{-9}$)
Cathode								
11.9	.92	3.26	22.2	.795	5.06	7.89	*44.1	*27.9
11.7	1.58	3.0	40.2	.558	5.75	9.15	*27.6	*17.4
11.3	1.24	2.14	37.5	.460	6.10	10.0	*21.1	*12.8
10.7	.84	1.95	26.5	.348	6.58	11.3	*14.3	* 8.3
10.1	.48	1.82	15.7	.208	8.95	16.1	* 6.52	* 6.8
9.3	.26	2.14	17.9	.130	11.35	18.8	* 3.21	* 1.95
8.3	.14	3.28	3.43	.124	11.75	19.4	* 2.95	* 1.87
7.3	.156	4.95	3.13	.171	9.70	16.0	* 4.95	* 2.99
1st Striation								
6.3	.072	6.51	1.24	.208	10.20	16.6	1.93	1.19
5.3	.132	8.7	1.98	.192	10.50	17.7	1.74	1.05
4.3	.120	9.15	1.75	.171	11.25	18.8	1.43	.86
3.3	.088	7.85	1.39	.166	11.50	19.2	1.36	.82
2.3	.080	8.5	1.21	.179	11.90	20.2	1.42	.84
2nd Striation								
1.3	.072	7.05	1.20	.166	12.20	20.9	1.29	.75
Anode								

TABLE III

Results for helium at .095 mm pressure. Length of discharge 10 cm $\overline{V}_+$ assumed to be .049 volts for all computations as the electric intensity is very small at all points given in the table. In this case, the positive column has not appeared in the region explored. Only the negative glow and cathode end of the Faraday dark space are present. Tube current 50 m.amps.

D (cm)	I_- ($\times 10^2$)	$\overline{V}$ (volts)	N_- ($\times 10^{-9}$)	I_+ ($\times 10^3$)	a_1 ($\times 10^2$)	a_2 ($\times 10^2$)	N_1^+ ($\times 10^{-9}$)	N_2^+ ($\times 10^{-9}$)
9.95				.195	21.5	31.8	2.55	1.72
9.9				.332	19.3	29.4	3.38	2.21
9.8				.312	15.9	27.4	5.52	3.19
9.6				.348	14.6	26.3	6.65	3.70
9.2	1.57	8.1	2.54	.296	13.0	24.3	6.40	3.41
8.4	2.16	7.85	3.40	.267	14.3	25.6	5.23	2.92
7.2	1.60	7.3	2.62	.238	15.2	26.2	5.38	2.51
6.0	1.68	7.85	2.64	.224	16.6	27.7	3.78	2.26
5.0	1.28	7.3	2.09	.251	15.4	26.8	4.39	2.62
4.0	1.08	7.6	1.73	.256	15.0	26.3	4.62	2.73
3.0	.50	7.85	.79	.243	15.7	27.4	4.41	2.48
2.0	.44	6.8	.74	.232	15.7	27.6	4.18	2.35
1.0	.28	7.05	.47	.229	15.3	26.8	3.98	2.38
.4	.26	7.2	.43	.195	16.7	27.9	3.25	1.96

TABLE IV

Comparison of the concentration of electrons with the current density of the discharge. Pressure was 2.9 mm., voltage across the tube was 83 volts and the length of the discharge 11.6 cm. D is the distance of the point from the anode in cm. N_{90}^- is the concentration with a discharge current of 90 m.amps. N_{180}^- is the concentration with a discharge current of 180 m.amps.

D	N_{90}^-	N_{180}^-
anode		
3.5 cm	7.6×10^9	16.8×10^9
5.0	7.6	14.8
6.0	4.7	11.4
7.0	5.6	11.6
9.0	16.5	26.0
10.0	42	90
10.5	123	280
11.0	336	660
11.3	300	520
cathode		

1. *Potential distribution.* Owing to the striation of the positive column, it was found that the potential gradient in the positive column was not uniform, but resembled in general that found in earlier work on mercury by one of us, and in hydrogen in recent work by Bramley.[9] The continuous curves in Figs. 2 and 3 show the potential distribution at two different pressures, 2.9 and 0.5 mm respectively.

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[9] Bramley, Phys. Rev. **26**, (Dec. 1925).

In the negative glow the potential gradient is very small or zero at higher pressures and is negative at lower pressures. The field gradually increases from the negative glow through the Faraday dark space to the positive column, reaches a maximum about the head of the positive column and falls off again inside the positive column. This also is in agreement with Bramley's results on hydrogen and the less conclusive results on mercury already referred to, and also with results on low voltage arcs in argon reported by Compton and Ekart.[10] This negative gradient is necessary in order to account for the observed currents in the discharge.

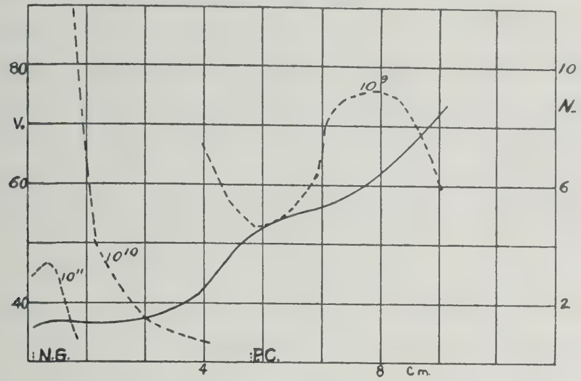

Fig. 2. Full curve represents potential distribution with ordinate given on left. Broken curve applies to electron concentration with ordinates given on the right multiplied by factors entered above each section of curve. Pressure 2.9 mm.

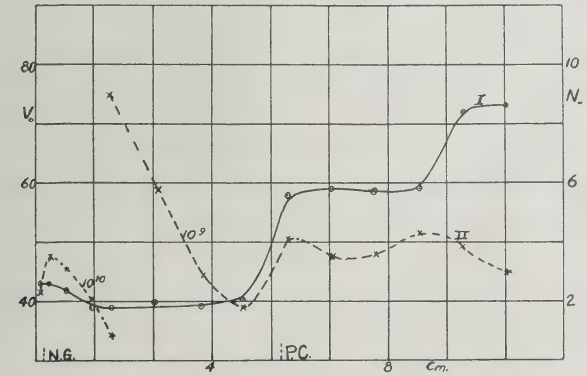

Fig. 3. Full curve represents potential distribution with ordinate given on left. Broken curve applies to electron concentration with ordinates given on the right multiplied by factors entered above each section of curve. Beginning of the negative glow is about N.G. and the positive column about P.C. Press. 0.5 mm.

[10] Compton and Ekart, Phys. Rev. **24,** 97 (1924).

2. *Average energy of electrons.* The average energy of the electrons was calculated from the $\log_e I$ *vs* V curves by Eq. (2). It was found that the average energy of the electrons was independent of the current density of the discharge but depended on the pressure of the helium. This was to be expected as it was found that the potential distribution was little affected by current strength and thus the average energy of electrons should also be independent of the current strength. Comparison between tables I, II and III shows that, at corresponding points of the discharge the average energy of the electrons increases with a decrease of pressure, except at points in the negative glow, in which case the increase in the current with the voltage in the curves from which the average energy is calculated is so rapid as to render accurate determinations of the average energy very difficult. It may therefore be stated that the average energy of the electrons in a given region of the discharge increases with a decrease of pressure. This is what should be expected from Compton's[11] equation for terminal velocities of electrons in a gas. Sufficiently accurate data have not been obtained however, to make numerical comparisons with Compton's equation.

3. *Electron Concentration.* The variation of the electron concentration with different factors in the discharge is closely related to the variation of the electron energy. Since the average energy has been found to be independent of current density in the discharge, the electron concentration should be proportional to the current carried by the discharge. By making determinations of the concentrations of the electrons at different currents, other conditions remaining constant, it was found that within the limts of accuracy of the experiments the concentration of the electrons was proportional to the current density of the discharge current. Results of this work are given in Table IV. Further, since the average energy was found to increase with a decrease of pressure, the concentration of electrons, necessary to produce a given current, should decrease with a decrease of pressure. Results given in Tables I, II and III appear to indicate that this is actually the case. As in the case of average energies, however, the experimental data are not sufficient, either in volume or accuracy, to enable a relation between pressure and concentration to be determined.

The mechanism of conduction, at best, must be complicated, since in all parts of the discharge we must have present in varying degrees both conduction and diffusion currents which together produce the observed discharge currents. Consequently a prediction as to how any factor should depend on any other must be based on very elaborate experimental data.

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[11] Compton, Phys. Rev. **22,** 334 (1923).

4. *Positive ion concentration.* It will be noted from the tables that the positive ion concentration has in all cases been calculated by the use of two different equations. In all cases but the last it may safely be assumed that Langmuir's space charge Eq. (4) cannot be expected to give accurate results as, on the average, the positive ions must suffer several collisions inside the space charge sheath. Further, Eq. (5) would appear to give a more reliable result, except possibly in the negative glow where the sheath thickness is not very large compared with the distance in which the positive ions attain .9 of their terminal energy, since the conditions of derivation of this equation are more nearly fulfilled than those underlying Langmuir's equation. The average electric intensity within the sheath is in all cases much greater than 100 volts per cm which would make the velocity of thermal agitation very small compared to that produced by the action of the electric field on the ion. Thus the values given under N_2 in tables I and II appear more reliable, while those under N_1 are probably more reliable in Table III.

In all cases the concentration of positive ions is very large in the negative glow and falls off towards the positive column. Inside the striations it has a varying value which follows closely the variations of the electron concentration. Also in the majority of cases the agreement in actual values between the electron and positive ion concentrations is fair. There is in no part of the discharge a great preponderance of ions of either sign, which must be true since the potential distribution shows no effect of large space charge at any point of the discharge, except within the cathode drop, which we could not explore by this method on account of its very small thickness.

Any data concerning positive ions must, at best, be only rough approximations. We have at present no method of determining directly the energy of the positive ions under the conditions which are maintained in the discharge and thus an error of 100 percent or more may occur. Thus the agreement found in this work appears satisfactory.

CONCLUSION

The results here reported appear to confirm, in some respects at least, the theory advanced by Compton, Turner and McCurdy,[8] in that the concentration gradient of electrons[12] is sufficient to account for the current in the negative glow and Faraday dark space. The negative potential gradient in the negative glow is found to occur at low pressures while at higher pressures the gradient is very small or zero. The observed negative gradients are of the order demanded by the kinetic theory of ionic diffusion. Also the cathode side of the striations appears to be a region of ionization and of positive space charge.

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[12] For a discussion of the necessary negative potential gradient in the negative glow reference must be made to the papers referred to above.[8] It is there pointed out that a

Sufficient data were not obtained to enable any numerical relations between average energy and concentration of electrons and the gas pressure to be established.

In conclusion, the authors wish to express their most sincere thanks to Professor K. T. Compton for his interest in the work, and valuable suggestions throughout the course of the investigation.

Palmer Physical Laboratory,
Princeton, N. J.
October 2, 1925.

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negative gradient in this region is necessary, since the current produced by the diffusion of electrons as calculated on the basis of the kinetic theory is larger than the observed current, thus a negative electron current is necessary to explain the observed facts.

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THE UNIVERSAL CONSTANT OF THERMIONIC EMISSION

By P. W. Bridgman

Abstract

Theoretical deduction of the formula for thermionic emission.—The constant A of the thermionic emission formula: $I=AT^2e^{-b_0/T}$ has been shown by Richardson and Dushman by different lines of argument to be a universal constant, and a value for the constant has been deduced by Dushman. The experimental data of Dushman verify this value of A for pure metals, but if the metal is coated there are very wide divergences. In this paper an attempt is made to give a more rigorous deduction of the emission formula, so that it may be plain under what conditions it may be expected that A be universal. Assuming that the entropy of the electron gas is the same as that of an ordinary monatomic gas in the Sackur Tetrode theory, and also assuming that the entropy of a surface charge is zero at 0° Abs. it is shown that an emission formula of the type above necessarily demands that A have the universal value assigned by Dushman, and the necessary and sufficient condition for this is that the difference between the specific heat of the neutral metal and of a charge on its surface vanish ($C_{pm}-C_{p\rho}=0$). This condition may also be formulated in terms of the surface heat and is equivalent to $\sigma+dP_s/dT-P_s/T=0$, where P_s is the surface heat and σ the Thomson heat. If σ can be neglected, the emission formula holds with the form given when P_s is proportional to absolute temperature.

Physically it seems probable that (1) if the metal is uncoated the forces on the surface ions are nearly the same as on the neutral atoms, so that the condition $C_{pm}-C_{p\rho}=0$ is satisfied, but (2) if the surface charge has the properties of a gas, as in an oxygen coated filament, (a) the specific heat may be different from that of the metal, or more probably (b) the entropy of the surface charge may not vanish at 0° Abs.; and (3) if the surface is coated with another more easily ionizable metal there may be electrical forces on the surface ions which modify their specific heat.

Introduction

In two recent papers Dushman[1] has given a theoretical deduction of the constant A of the formula of thermionic emission

$$I=AT^2e^{-b_0/T}$$

and has discussed the agreement with experiment in the light of new and more accurate data. The deduction of the value of A involves the Sackur-Tetrode theory of the entropy constant of a monatomic gas (which here is the electron gas in contact with the metal), and the value found by Dushman is $A=2\pi k^2m\epsilon/h^3$.

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[1] S. Dushman, Phys. Rev. **21,** 623-636 (1923); **25,** 328-360 (1925).

In a note commenting on the first paper of Dushman, Richardson[2] points out that as early as 1915 he had, by a purely thermodynamic argument not involving quantum theory, shown that A is a universal constant, and had even gone further, and by an argument involving quantum theory, had found the factors $k^2m\epsilon/h^3$ in A, but with a numerical coefficient different from 2π.

Experimentally Dushman found that the formula is entirely satisfactory for tungsten, for which the experimental data are most accurate, and probably is satisfactory for molybdenum and tantalum, for which the data are less accurate, but that if the emitting substance is not a pure metal, but is coated, the values of A range from 5×10^{11} to 3×10^{-3} (1925 paper, page 358). It would appear, therefore, that the arguments of both Dushman and Richardson must neglect some factor which is not important for pure metals, but which may be very important indeed in the more general case to which their arguments apply at least by implication.

Dushman states that his theoretical deduction of A neglects the surface heat, and that the agreement of the formula for tungsten indicates that for this metal the surface heat is small. Dushman, however, does not show at all in detail how the surface heat is concerned in the deduction of the formula, so that although we may be willing to accept his statement that the formula could be obtained by neglecting the surface heat, it is not at all obvious that conversely we may infer that, if the formula holds, the surface heat must be zero. The question of the surface heat was discussed by me at considerable length in the Physical Review[3] several years ago. It is a reversible heat which must be added or subtracted when an electrical charge is applied to or removed from the surface of a conductor isothermally. The possible existence of this surface heat has been neglected in nearly all thermodynamic discussions of this subject.

The original and fundamental thermodynamic discussion of Richardson has been recognized for some time to be lacking in rigor because of his interchangeable use of quantities thermodynamically different. Schottky pointed this out in 1915,[4] and I also discussed the matter at some length[3] (without knowledge of Schottky's work, which was inaccessible because of the war), and gave corrected forms for several of Richardson's formulas. Richardson has recently recognized[5] that he did neglect the difference between two quantities really different, but his present position is that as a matter of experiment the difference is small, and he points to recent experiments on tungsten as justification. He characterizes as "severe" my criticism that "the neglect of the surface heat in Richardson's equation would therefore seem to be indefensible, and until the order of the effect is known we cannot tell whether Richardson's equation is even approximately correct." In view of possible experimental variations from 5×10^{11} to 3×10^{-3} it does not seem to me that this remark is "severe."

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[2] O. W. Richardson, Phys. Rev. **23,** 153-155 (1925).

[3] P. W. Bridgman, Phys. Rev. **14,** 306-347 (1919).

[4] W. Schottky, Verh. D. Phys. Ges. **7,** 109-121 (1915).

[5] O. W. Richardson, Proc. Roy. Soc. **105,** 403 (1924).

It is the purpose of this paper to present a derivation of the thermionic emission equation without the approximations of either Richardson or Dushman, to find under what conditions the formula reduces to the simple form given, and in particular what are the necessary assumptions about the surface heat, and finally to discuss what may be the physical basis for the evident difference between the value of A for coated and uncoated conductors.

DEDUCTION OF THE THERMIONIC EMISSION FORMULA

It must in the first place be said that it is recognized by everyone that there is an uncertain element in the formula for thermionic emission current in that it is necessary to assume no reflection of electrons on impinging on the metal surface from the gas. Thermodynamically we can find only the density (or pressure) of the electron gas in contact with the metal under equilibrium conditions. To pass from electron density to saturation current involves kinetic theory, assuming Maxwell's distribution of velocity, and also the assumption of no reflection.[6] In the following discussion we consider, instead of the emission current, the electron gas pressure. Under the usual assumptions of kinetic theory Dushman's formula is then equivalent to

$$p=\frac{(2\pi m)^{3/2}k^{5/2}}{h^3}T^{5/2}e^{-b_0/T}$$

where p is the density of the electron gas at points immediately outside the metal, and the significance of the other letters is the conventional one. (I shall assume here as known and accepted the results of the long discussion between Schottky and v. Laue as to the justifiability of treating the electron atmosphere as a perfect gas.)

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[6] In this discussion no consideration is to be given to the somewhat modified form of the universal constant which would be obtained if the theory of G. N. Lewis of ultimate rational units is accepted. In view of the considerable uncertainty arising from the effect of electron reflections at the surface, I do not believe that any measurements of the saturation current are able at present to distinguish between the two values of the constant.

It should also be said that the new ideas about the entropy constant of a monatomic gas were first applied to the electron vapor by v. Laue,[7] who obtained a value for p in which the coefficient of the exponential term is exactly that of Dushman, but which has the exponential term $e^{-\mu/RT}$. Here μ is the so-called "electron affinity" of the electron for the metal. v. Laue explicitly recognized and stated that μ may be a function of temperature. If there are terms in μ proportional to the temperature the universal constant will obviously be modified, and in any event the formula does not reduce to that above unless μ is a constant. Physically, "electron affinity" is a concept most difficult to interpret in terms of quantities directly measurable, so that the formula as given by v. Laue actually becomes an equation for finding "electron affinity" in terms of emission data, and is therefore not adapted to our purposes, although from the thermodynamic point of view no criticism can be made of the rigor of the deduction.

Given now a neutral metal at 0° Abs. We raise it, in the neutral condition, to the temperature T, and at this temperature evaporate from it reversibly at the equilibrium pressure a certain number of electrons, leaving behind on the surface of the metal in the form of surface charge an equal and opposite positive charge. The final system consists of electron vapor, surface charge, and remaining neutral metal. For the purposes of this argument we may imagine that all the neutral metal is evaporated, leaving a final system of only vapor and surface charge. The entropy of the final system is the sum of the entropy of the gas and of the surface charge. If we accept the dictum of the third law that the entropy of the neutral metal is zero at 0° Abs., the entropy of the final system is also equal to the entropy imparted to the neutral metal on warming from 0° Abs. to T plus the entropy change during evaporation. The entropy of the electron gas per electron is

$$s_0+(5/2)k\log T-k\log p$$

where, according to the Sackur-Tetrode theory s_0 has the value:

$$s_0=k\left(5/2+\log\frac{(2\pi m)^{3/2}k^{5/2}}{h^3}\right)$$

The entropy change of the system during evaporation is η/T, where η is the latent heat of evaporation per electron, *the system being isolated so that during the evaporation a compensating surface charge is left on the metal.* The entropy change of the neutral metal during heating is

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[7] M. von Laue, Jahrb. d. Rad. u. Elek. **15**, 257-270 (1918).

$\int_0^T (C_{pm}/T)dT$, where C_{pm} is the specific heat at constant pressure of that number of atoms of the neutral metal which give rise to one electron of vapor. The entropy of the surface charge, assuming that the surface charge acts like a condensed system so that its entropy at 0° Abs. vanishes, is $\int_0^T (C_{pp}/T)dT$, where C_{pp} is the specific heat at constant pressure of the surface charge left when one electron evaporates. Equating these entropies gives

$$\eta/T + \int_0^T (C_{pm}/T)dT = k\left(5/2 + \log\frac{(2\pi m)^{3/2}k^{5/2}}{h^3} + (5/2)\log T - \log p\right) + \int_0^T (C_{pp}/T)dT\,.$$

This equation may be solved for p, giving

$$p = \frac{(2\pi m)^{3/2}k^{5/2}}{h^3} T^{5/2} e^{5/2 - \eta/kT + (1/k)\int_0^T [(C_{pp}-C_{pm})/T]dT}.$$

In this expression everything except the exponential is of the form deduced by Dushman. Our immediate problem is then to find under what conditions the exponent reduces to $-b_0/T$. We must in the first place use what information we have about η, which is a function of temperature. One relation is immediately obtained from general thermodynamics. We have for the latent heat of any transition

$$\frac{d\eta}{dT} = \frac{\eta}{T} - \frac{\eta}{\Delta v}\left(\frac{\partial \Delta v}{\partial T}\right)_p + \Delta C_p.$$

Here Δv is the change of volume during the transition, and ΔC_p is the difference between the specific heat of the system before and after the transition. Applied to the electron vapor, we may in the first place neglect the volume of the metal and surface charge compared with the volume of the vapor, putting $\Delta v = v = (kT/p)$. ΔC_p, which for usual systems consist of only two terms, here consists of three terms, arising from the gas, the surface charge, and the neutral metal.

$$\Delta C_p = C_{pg} + C_{pp} - C_{pm}\ .$$

For a monatomic gas $C_{pg} = (5/2)k$. Substituting these values gives

$$\frac{d\eta}{dT} = \Delta C_p = (5/2)k + C_{pp} - C_{pm}\ ,$$

which gives on integrating

$$\eta = \eta_0 + (5/2)kT + \int_0^T (C_{pp} - C_{pm})dT\ .$$

Substituting back in the value for p, we obtain

$$p=\frac{(2\pi m)^{3/2}k^{5/2}}{h^3}T^{5/2}e^{-\eta_0/kT-(1/kT)\int_0^T(C_{p\rho}-C_{pm})dT+(1/k)\int_0^T(1/T)(C_{p\rho}-C_{pm})dT}.$$

Now to find under what conditions the exponent has the desired form, we put

$$-\eta_0/kT-(1/kT)\int_0^T(C_{p\rho}-C_{pm})dT+(1/k)\int_0^T(1/T)(C_{p\rho}-C_{pm})dT=-b_0/T.$$

Differentiate by T, giving

$$\eta_0/kT^2+(1/kT^2)\int_0^T(C_{p\rho}-C_{pm})dT=b_0/T^2.$$

Multiply by T^2 and differentiate again, giving

$$C_{p\rho}-C_{pm}=0.$$

Hence we see that the vanishing of $C_{p\rho}-C_{pm}$ is a necessary and sufficient condition for the formula found by Dushman with his value of the constant. We may go further and inquire under what conditions the formula takes the form $A'T^{5/2}e^{-b_0/T}$ where A' is some constant different from that above. The question is at once answered like that above by putting the exponent equal $-b_0/T+Const.$ Differentiation, as before, again shows that $C_{p\rho}-C_{pm}=0$, so that we conclude that if the expression $A'T^{5/2}e^{-b_0/T}$ holds, both $C_{p\rho}-C_{pm}$ must vanish, and A' must have the universal value above.

The conclusions of the last paragraph have involved the assumption that the surface charge acts like a condensed phase in so far as to have zero entropy at 0° Abs. If this condition is not satisfied, there will be a constant in the exponent, so that there results a formula $A'T^{5/2}e^{-b_0/T}$ with a value for A' different from the universal constant above.

That Dushman has essentially neglected the term $C_{p\rho}-C_{pm}$ may be seen by a detailed examination of his argument, particularly his equation (2) on page 624, and his remarks at the bottom of page 624 and top of page 625.

The conditions under which the general formula with the accepted universal constant is valid have thus far made no mention of the surface heat. The connection may now be shown as follows. Equation (28) of my previous paper,[3] deduced by cyclic operations suggested by Richardson's analysis and entirely different from any used in deducing the previous value of $d\eta/dT$ is equivalent to the equation

$$d\eta/dT=(5/2)k-\epsilon(\sigma+dP_s/dT-P_s/T).$$

Here P_s is the heat which must be absorbed by the system to maintain it isothermal when one unit of electricity is added to the surface, and σ is the Thomson heat as ordinarily defined. Equating the two values of $d\eta/dT$ gives

$$C_{pm}-C_{pp}=\epsilon(\sigma+dP_s/dT-P_s/T) \ .$$

Hence the assumption implicitly contained in the argument of Dushman, and also in that of Richardson as far as its application to the present problem is concerned, is equivalent to setting $\sigma+dP_s/dT-P_s/T$ equal to 0. Now it is generally considered that σ is small compared with other terms in problems of this character, so that if we neglect it the condition reduces to $dP_s/dT-P_s/T=0$, which demands that P_s be proportional to temperature.

It is therefore not necessary that the surface heat vanish in order that the emission formula hold; numerically it may be large or small provided only that it be proportional to temperature.

PHYSICAL SIGNIFICANCE OF THE CONDITIONS

Returning now to the condition expressed in the form $C_{pm}-C_{pp}=0$, the experimental data obtained by Dushman suggest that the specific heat of the ionized atoms which constitute the surface charge is the same as that of the neutral metal atoms if the metal is pure, but different if the metal is coated. What may we conceive to be the physical reason for this? If the metal is pure the surface charge consists of ionized atoms scattered about in the surface layer of the crystal lattice of the metal, which reaches to the surface without alteration. The analysis of v. Laue has shown that if the electron vapor is to be treated as a perfect gas and the effect of space charge neglected, the electron vapor can occupy a space only a few free paths thick. Under these conditions the distance between the ions in the surface layer is of the same order of magnitude as that between the electrons in the vapor, and since the electrical forces between the electrons in the vapor are negligible under these conditions, it must also be true that in the surface layer the mutual electrical forces between the ions are negligible compared to the forces holding the ions in the crystal lattice. The natural frequency of the surface ions is then approximately the same as that of the surface atoms, and the specific heat is therefore the same.

If, however, the metal is coated, these conditions no longer hold and we may have various sorts of behavior. If the surface coating has approximately the properties of a gas, as in an oxygen coated filament, the surface atoms have the specific heat of a gas atom, which is only half that of an atom in the solid at high temperatures, but greater at low temperatures. Or, which seems to me much more probable under these conditions, the failure of the formula may be due to the non-vanishing of the entropy of the surface charge at 0^0 Abs. If on the other hand the coating is another metal, particularly if it is one more easily ionized than the underlying metal, the surface charge will consist of ions of the coating metal. If there is any tendency for the coating atoms to bunch themselves on the surface, the ions to which they give rise will be subject to mutual electrical forces which may modify the specific heat.

One is tempted to try for further information about the precise behavior of $C_{pm}-C_{pp}$ in those substances for which the constant of the emission formula has not the universal value above. This, however, is probably not possible with present experimental data. Our argument above has suggested that $AT^2e^{-b_0/T}$ cannot be the correct form of the emission formula under these conditions, but that this form is only an approximation. Before we can reason back to the behavior of the specific heats we must know the correct form of the function. It is presumably impossible to do this with sufficient precision until experimental accuracy is very greatly improved, as is suggested by the fact that until very recently it was impossible to decide whether a formula with T^2 or $T^{\frac{1}{2}}$ fitted better the experimental data.

The Jefferson Physical Laboratory,
Harvard University, Cambridge, Mass.
November 15, 1925.

THE DIELECTRIC CONSTANT AND MOLECULAR WEIGHT OF BROMINE VAPOR

By Linus Pauling*

Abstract

It is shown that the conclusion reached by Bramley in a recent article that bromine has the formula $(Br_2)_6$ is inconsistent with previous results relating to the density of this substance in the gaseous state and that it is not theoretically justified by the considerations presented by the author.

In a recent paper entitled "Measurements of Velocity of the Synthesis of Hydrogen Bromide by Capacity Change" Arthur Bramley[1] has reported that his experiments lead to a value of 1.0128 (reduced to 0° and 1 atm.) for the dielectric constant of bromine vapor, from which he draws the conclusion that bromine has the formula $(Br_2)_6$. Assuming that bromine vapor consists of diatomic molecules, he calculates from Lorentz's formula $\kappa-1=C\rho$, where ρ is the density and C a constant evaluated from measurements on liquid bromine, that the dielectric constant κ should be 1.0022. Furthermore, from the index of refraction n of bromine vapor, 1.00115 (reduced to 0°C. and 1 atm.) and the equation $\kappa=n^2$, he finds a nearly equal value 1.0023. Since his observed value of $\kappa-1$ is almost six times that calculated for Br_2, he concludes that bromine vapor must have the formula $(Br_2)_6$.

This conclusion is, however, not in accord with density investigations. In an extensive series of vapor-density experiments, E. P. Perman[2] has shown that except at very high temperatures bromine vapor consists entirely of diatomic molecules. Vapor-densities (referred to that of hydrogen as unity) from one series of experiments at 14.7-15° are given in the accompanying table.

Pressure in mm.	98.65	63.70	32.10	16.65
Vapor-density	80.3	80.4	81.3	83.3

Professor Perman concludes "These results show that, on approaching the liquid state, bromine has no tendency to form molecules with more than two atoms. This agrees with the results of Paterno and Nasini[3] by Raoult's method, which indicated molecules Br_2 in aqueous and acetic acid solutions." He further states that experimental errors account for the apparent increase in vapor-density at very low pressures; this increase of course could not be adduced as evidence of the formation of molecules with more than two atoms, for this would contradict the principle of Le Chatelier.

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* National Research Fellow in Chemistry.

[1] A. Bramley, Phys. Rev. **25**, 858 (1925).

[2] E. P. Perman, Proc. Roy. Soc. **48**, 45 (1890).

[3] Paterno and Nasini, Deutsch. Chem. Ges., Ber. **21**, 2153. (1888).

The value reported by Bramley for the dielectric constant of bromine vapor is surprisingly high, in view of the fact that diatomic bromine molecules presumably do not have large electric moments. It is unfortunate that the investigator published none of his experimental data on capacity measurements and determinations of the partial pressure of bromine, which would have permitted checks on his calculations. It seems probable that the value 1.0128 is incorrect because of large experimental errors, for the capacity measurements represented in the graphs were subject to remarkably large fluctuations, amounting, in fact, in some cases to as much as fifty percent of the total change produced by the reaction. The investigator attributed these fluctuations in his measurements to variations in the amounts of bromine vapor present as Br_2 and as $(Br_2)_6$. Since $(Br_2)_6$ is probably not present this explanation is of course unsatisfactory; even if it were present, familiar statistical mechanical considerations indicate that such enormous fluctuations could not be expected to occur in a chemical equilibrium involving such a large number of molecules.[4]

This uncertainty concerning the experimental work throws doubt also on the final conclusion reached by the investigator that the specific photochemical rate for the chemical reaction considered has a negative temperature coefficient.

California Institute of Technology,
Pasadena, California.
November 20, 1925.

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[4] That such fluctuations in a chemical equilibrium do not occur is at once evident if one considers their influence for example on the pressure of the system. From Fig. 2 of Bramley's paper it is seen that the measured capacity of the cell had for a period of two minutes a value greater than the equilibrium value by an amount of over 15% of the total change corresponding to the complete combination of hydrogen and bromine to form hydrogen bromide. Since the capacity measurements are made on all the gas between the two plates in his cell, this result requires that if the volume of the gas (about 1 cc) were kept constant, the pressure would show variations due to the postulated fluctuations from the equilibrium state. As there is liquid bromine present the pressure is at least 150 mm; hence the explanation of his observations advanced by Bramley would require that pressure variations greater than 20 mm and lasting more than two minutes occur in this system. This is, however, obviously not possible; we are led to accept the alternative explanation that the variations are due to experimental error.

PHYSICAL REVIEW FEBRUARY, 1926 VOL. 27

TEMPERATURE COEFFICIENT OF MAGNETIC PERMEABILITY OF SHEET STEEL

By T. Spooner

Abstract

The samples tested were annealed punched rings of commercial sheet steel such as is used in electrical apparatus, containing 0.9 to 4 percent silicon. Temperature coefficients were determined in the range from −20° to +46°C. As the induction was increased from 2 to 10 kilogausses, the coefficient decreased from +.12% per 1°C to −.021% for 0.9% Si, from +.08% to −.08% for 2.2% Si, and from −.03% to −.18% for 4% Si. Each curve showed a minimum at 10 kilogausses although the maximum permeability normally occurs at 6 to 8 kilogausses. This minimum corresponds to 2 gilberts per cm and is sharper the higher the Si content. These results indicate that the temperature coefficient is more directly related to the induction than to the permeability.

MUCH information is available concerning the relation between temperature and the magnetic properties of ferro-magnetic materials. This is particularly true with reference to permeability. In general, however, these published data deal either with a large range of temperature or with the properties at fairly high temperatures where the thermo-magnetic transformations take place. The available information over small ranges in the region of room temperature is very meager.

Burrows[1] states that permeability at room temperature increases with temperature for low inductions and decreases for high. He also states that the change in induction for 1°C rise in temperature is greatest in the neighborhood of the maximum permeability.

Sanford[2] has given the most complete data of which we have knowledge for the temperature permeability characteristics in this region. Tests were made on samples of cast iron, wrought iron and low-carbon steel for a temperature range from 3° to 88°C and for magnetizing forces up to 200 gilberts per cm. Test results are given for various heat treatments. Some samples showed a positive temperature coefficient of permeability, some a negative and some a change of sign as the induction increased. In one or two cases the sign of the temperature coefficient was changed by heat treatment.

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[1] C. W. Burrows, Bull. Bureau of Standards, Vol. **4,** p. 205 (1907).

[2] R. L. Sanford, Bull. Bureau of Standards, Vol. **12,** p. 1-10 (1915).

No one, apparently, has dealt adequately in the room temperature range with the temperature-permeability characteristics of sheet steel such as is used in electrical apparatus. These characteristics are of importance in connection with theories of magnetism and from a practical standpoint in connection with the performance of electrical measuring instruments which use ferro-magnetic material in the magnetic circuit, such as watt-hour-meters.

This paper gives some test results which have been obtained on commercial electrical sheet for a range of temperatures from −20°C to +46°C. Because the values of the temperature coefficients in the room temperature range are small and other effects such as incomplete demagnetization may produce as large or larger changes of magnetic permeability than the temperature changes, great care has to be exercised if accurate data are to be obtained.

Test samples. The samples consisted of punched rings $1\frac{3}{4}$ in. (3.44 cm) o.d. and $1\frac{1}{4}$ in. (3.17 cm) i.d., annealed at about 800°C before testing. There were four samples of .9 percent silicon sheet, .0172 in. (.0437 cm) thick, four samples of 2.2 percent silicon sheet, .014 in. (.0356 cm) thick, and three samples of 4 percent silicon sheet .014 in. thick. Each sample consisted of about 110 grams of rings and each was provided with 170 secondary turns and a common primary of 10 turns. Results are also included for a 2.2 percent and a 4 percent silicon sample consisting of rings 3 in. o.d. and 2 in. i.d. which had been tested previously.

Test methods. The samples were placed in a double kerosene bath, the outer part of which was heated by an electrical resistance or cooled by means of CO_2 snow. The magnetic tests were made by a null method using a variable mutual inductometer and fluxmeter. The primary current in the inductometer and the current in the primary of the samples were reversed simultaneously and the mutual inductometer adjusted until the fluxmeter in series with the secondary windings showed no residual deflection. For a given temperature the magnetizing force was adjusted to a definite value, and with the aid of a transfer switch, the corresponding induction was measured successively for each sample. The m.m.f. was then increased and the process repeated. For $B = 10$ kilogausses the induction was kept constant and the current changed. Samples were carefully demagnetized before testing and were put through the cycle many times (100 or more) for each m.m.f. before readings were taken. A change of 0.1 percent in induction could readily be observed, at least for the higher values.

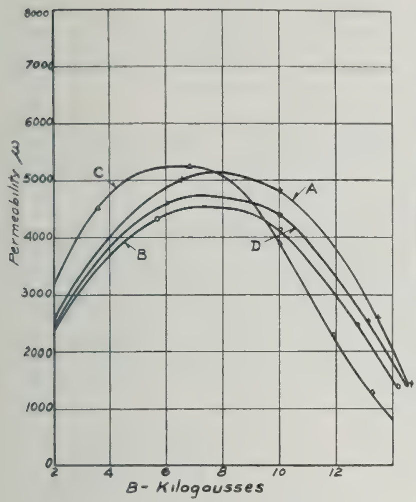

Fig. 1. 0.9% silicon sheet steel.
Normal permeability.

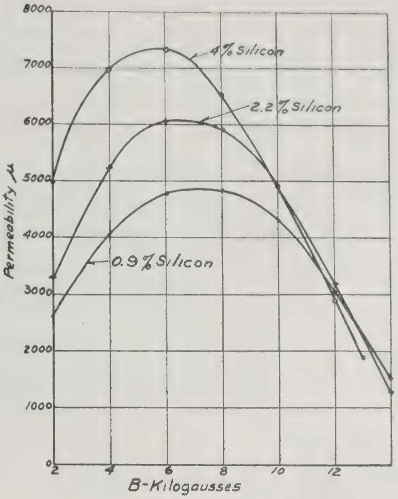

Fig. 2. Electrical sheet steel.
Mean permeability.

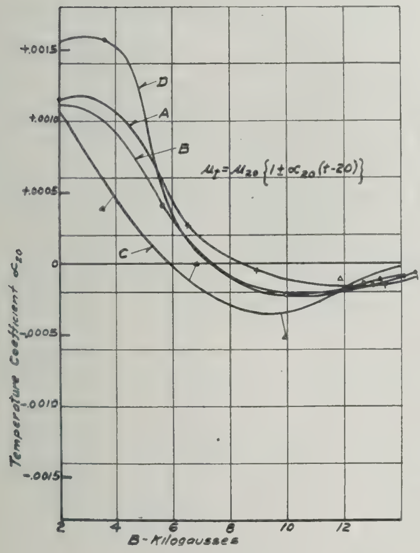

Fig. 3

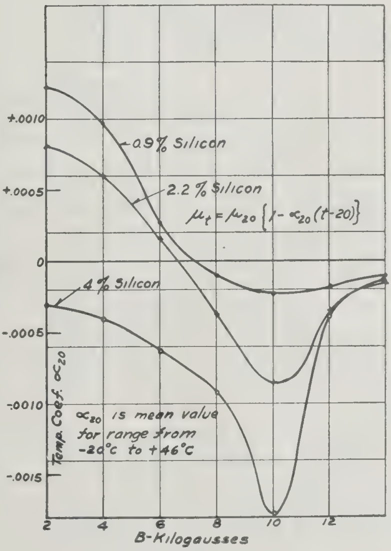

Fig. 4

Fig. 3. 0.9% silicon sheet steel. Temperature coefficient of magnetic permeability as a function of induction, based on the permeability at 20°C.

Fig. 4. Electrical sheet steel. Temperature coefficient of magnetic permeability as a function of induction, based on the permeability at 20°C.

Test results. Fig. 1 shows the permeability values as a function of induction for the four .9 percent silicon steel samples. The letters refer to different samples. Similar curves, not shown, were obtained for the medium and high silicon material.

Fig. 2 shows the average permeability curves for the three classes of material. The medium and high silicon steel curves include the permeability results for the two larger ring samples.

The permeability values for a given sample corresponding to a definite m.m.f. or induction were measured at temperatures of −20, +1, +24.8 and +46°C. The results were plotted against temperature and the best straight line drawn. This assumes that the permeability changes linearly with temperature between −20°C and +46°C. Within the accuracy of test this was the case.

The temperature-permeability curves are undoubtedly not straight lines but due to inaccuracies in testing and to the comparatively small temperature range the departures from straight lines are so uncertain that this assumption is probably as reliable as any which could be made from the available data.

From these straight lines the 20° temperature coefficients α_{20} were calculated from the formula,

$$\mu_t = \mu_{20}(1 \pm \alpha_{20}(t-20)) \qquad (1)$$

where μ is the permeability for any temperature t between −20 and +46°C, μ_{20} is the 20°C permeability.

Fig. 3 gives the temperature coefficients for the .9 percent silicon steel samples plotted against maximum induction.

Fig. 4 gives the mean temperature coefficient values for the three classes of material plotted against maximum induction. The data for the large samples are included.

Fig. 5 gives the same data plotted against maximum magnetizing forces.

Fig. 6 gives the average permeability in percent of the 20°C values plotted against temperature for the three classes of material and for a maximum induction of 10 kilogausses. Since the maximum negative temperature coefficient occurs at about 10 kilogausses, these lines have approximately maximum negative slope. For other inductions the slopes will be less or in the case of medium and low-silicon steels the the slopes will reverse for the lower inductions.

Discussion of results. It will be seen from Fig. 3 (and this is corroborated by data not shown) that the samples for a given grade of material all have about the same temperature coefficient characteristics. The

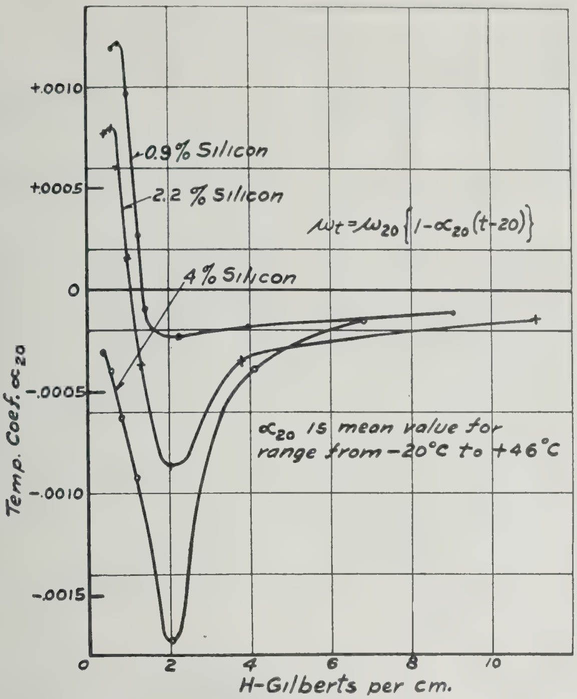

Fig. 5. Temperature coefficient of magnetic permeability as a function of magnetizing force, based on the permeability at 20°C.

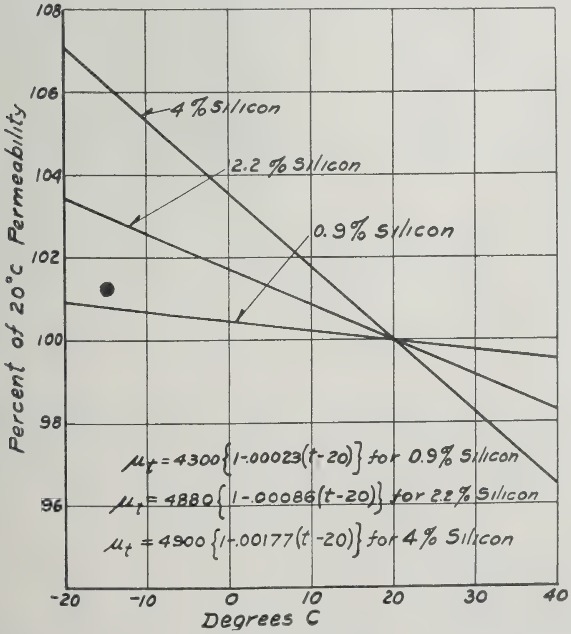

Fig. 6. Electrical sheet steel. Change in permeability due to temperature, based on permeability at 20°C. $B_m = 10$ kilogausses.

large samples show slightly different characteristics, particularly in the case of the 4 percent silicon steel. This may be due to the fact that the effect of punching alters the temperature coefficients, even after annealing.

The change of sign of the temperature coefficients with induction is common to many types of ferro-magnetic materials. The cause is an interesting subject for speculation. It might be expected that the maximum negative temperature coefficients would occur at the same inductions as those at which the maximum permeability occurs or at least that the temperature coefficient curves against the flux density would show some definite change corresponding to these inductions. However, this does not seem to be the case. There seems to be no definite relation between permeability and temperature coefficient. The maximum negative temperature coefficients correspond quite definitely to approximately 10 kilogausses whereas the maximum permeabilities occur at about 6 or 7 kilogausses.

Conclusions. From these data and others not included, the following conclusions may be drawn.

1. Low and medium silicon steels have large positive permeability temperature coefficients for low inductions and negative coefficients for high (up to 14 kilogausses). Four percent silicon sheet on the average has negative coefficients for all inductions (up to 14 kilogausses) though individual samples may have small positive coefficients for low inductions.

2. As the silicon content increases, the coefficients tend to move in a negative direction. This may be due to the direct influence of the silicon or to an indirect influence of the silicon on the carbon and other impurities.

3. The shape of the temperature coefficient curves seems to be much more definitely a function of the induction than of the m.m.f., since the maximum negative temperature coefficients correspond very definitely to a certain induction but may vary over a considerable range of m.m.fs.

4. There seems to be no definite relation between permeabilities and temperature coefficients for the individual samples of a particular grade of material and no definite relation between the inductions at which maximum permeabilities and maximum temperature coefficients occur.

Westinghouse Research Laboratory,
East Pittsburgh, Pa.
September 10, 1925.

PHYSICAL REVIEW FEBRUARY, 1926 VOL. 27

THE PROPAGATION OF RADIO WAVES OVER THE EARTH

By A. Hoyt Taylor and E. O. Hulburt

Abstract

Theory of radio wave propagation over the earth.—Larmor's theory of refraction due to the electrons of the Kennelly-Heaviside layer does not explain the "skip distances" for short radio waves (regions of silence around the transmitter which Taylor's measurements showed to be 175, 400, 700 and 1300 miles in radius in the daytime for waves of 40, 32, 21 and 16 meters, respectively, and which are surrounded by zones of strong signals). The range as a function of wave-length shows a minimum for about 200 meters which suggests the introduction of a critical frequency term. If the effect of the magnetic field of the earth on the motion of the electrons is taken into account, as suggested by Appleton and by Nichols and Schelleng, the modification of the Larmor theory necessary to fit it to the experimental facts is secured. A quantitative theory is here developed. The upper atmosphere is assumed to contain N free electrons per cc., and neglecting absorption the dispersion equations are worked out for various modes of polarization of the radio waves. Then the skip distances are computed, making various assumptions as to the electron density distribution. (a) Reflection theory. As a first approximation the layer is taken to be sharply separated from the un-ionized lower atmosphere. At this layer total reflection occurs in accordance with Snell's law. (b) Refraction theory. The following distributions are considered: (1) Density increasing linearly with the height h, beginning at a certain height h_0; (2) Density proportional to h^2; (3) Density proportional to e^h; (4) Density proportional to $h^{\frac{1}{2}}$. Comparison with the experimental skip distances shows good agreement, and indicates that the radio waves which just reach the edge of the zone beyond are refracted around a curved path, reaching in the daytime a maximum height of from 97 miles (case 1, $h_0=21$ miles, and case 2) to 149 miles (case 3). At this height the electron density comes out close to 10^5 electrons per cc. At night the electron density gradient is less and the height is greater. These conclusions agree with physical conceptions from other evidence. From the dispersion equations it follows that for waves of 60 to 200 meters, total reflection may occur from the electron layers at all angles of incidence. From this result, combined with interference between various modes of polarization of the radio rays, a detailed qualitative explanation of many fading phenomena is presented. Further conclusions are: That the ions in the atmosphere have little effect in comparison with the electrons; that for longer waves, the Larmor theory is correct; that short waves are propagated long distances by refraction in the upper atmosphere and reflection at the surface of the earth, not by earth-bound waves; that waves below 14 meters cannot be efficiently used for long distance transmission.

Introduction

THE conception that upper regions of the atmosphere of the earth relatively richer in ions and electrons than the lower levels may play an important role in the propagation of radio waves over the earth has become more firmly established with the years. It is the purpose of this paper to develop the conception in greater detail than perhaps has been done up to this time and to discuss the conclusions quantitatively in the light of new experimental observations on the transmission of short radio waves over long distances. The first suggestion[1] of ionized atmospheric layers in connection with radio waves was, as far as we know, published by Kennelly.[2] Heaviside[3] set forth similar ideas independently a few months later. We have therefore thought it correct to speak of the ionized layer as the "Kennelly-Heaviside layer," although the designation "Heaviside layer" has been widely used in the literature of radio.

Although no complete summary of the researches on electric wave propagation will be attempted here, a few of the more important steps may be outlined briefly. Our experimental knowledge of the variation of the strength of the received signal as the distance from the transmitting station is increased is due largely to the work on waves longer than 500 meters carried out in 1910 and 1913 by the United States Navy under the direction of Austin.[4] The results are usually expressed by the well-known Austin-Cohen formula, which showed, in particular, that the intensity of the received wave fell off faster than the distance from the source than would be required by a simple inverse square law. The mathematical researches of Nicholson,[5] Love,[6] and Van der Pol,[7] Macdonald,[8] Watson,[9] and others have led to the conclusion that a simple theory of diffraction of the waves around an earth of finite, or infinite, conductivity immersed in a limitless dielectric yielded an intensity decrement factor very much greater than the experimental factor of the Austin-Cohen formula. In order to obtain agreement with observations the presence of converging waves was necessary, which meant that a portion, at least, of the waves must be reflected or refracted downward from the ionized upper reaches of the atmosphere. This was in strong support of the Kennelly-Heaviside conception which just at that time had been given a more definite formulation by

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[1] See L. Bouthillon, L'Onde Électrique **2,** 345 (1923).

[2] Kennelly, Electrical World and Engineer, p. 473 (March 15, 1902).

[3] Heaviside, Encyclopædia Britannica, Tenth Edition, Ninth Volume (No. XXXIII), p. 215 (December 19, 1902).

[4] Austin, Bull. Bur. Stand., **7,** 317 (1911).

[5] Nicholson, Phil. Mag. **22,** 157 (1910); **21,** 62 (1911).

[6] Love, Phil. Trans. Roy Soc. A, **215,** 105.

[7] Van der Pol, Phil. Mag. **38,** 365 (1919).

[8] Macdonald, Proc. Roy. Soc. **71A,** 251 (1903).

[9] Watson, Proc. Roy. Soc. **95A,** 546 (1919).

Eccles.[10] Eccles assumed an upper layer so intensely ionized as to reflect the rays without penetration, combined with an ionization of the middle atmosphere which bent them, and in his treatment dealt only with the motions of the heavy ions. It has remained for Larmor[11] in an interesting paper of accustomed clarity, to sketch a theory of refraction due largely to the free electrons. These were shown to be of such long free path as to exert a negligible absorption on the waves passing through them. Being lighter than the ions of Eccles only comparatively few electrons were necessary to produce sufficient bending of the rays.

At the end of the year 1924 it appeared that a reasonable and adequate theory of radio wave propagation had been rounded out, as yet qualitative to be sure, but requiring only obvious measurements to be placed on a quantitative basis. At this satisfactory stage, as has often happened before, new phenomena made their appearance which the theory was unable to cope with. Larmor's equations gave a refraction which decreased with the wave-length becoming small for waves below 60 meters, whereas the work of Reinartz[12] and Taylor[13] on the "skip distance" for waves below 60 meters immediately indicated a stronger refraction than for the long waves. Fortunately, at this time Appleton[14] pointed out that the free electrons would move in spiral paths at a specified frequency because of the magnetic field of the earth, and that perhaps peculiar effects would occur for waves near this frequency. This meant of course the introduction of a critical frequency term into the refraction equation, which produced exactly the modification required, i. e., it left Larmor's equations (which had neglected the magnetic field of the earth) approximately unchanged in the region of longer waves and brought the theory into agreement with the short wave data. It may be mentioned that we had already independently introduced a critical frequency term into the classical dispersion formula used by Larmor, basing the idea on the curve of Fig. 2, without however troubling as to the physical cause of the term. From Appleton's suggestion it was immediately possible to apply the classical formulas of magneto-optics to the Kennelly-Heaviside layer. While this was in progress the paper of Nichols and Schelleng[15] appeared in which similar ideas, again of independent origin, were taken up. However, this paper and theirs do not cover the same ground, for in their paper no quantitative applications of the formulas to observations were made. The publication of this paper* has been delayed until the results of the observations on the secondary skip distances were available.

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[10] Eccles, Proc. Roy. Soc. **87A,** 79 (1912).

[11] Larmor, Phil. Mag. **48,** 1025 (December, 1924).

[12] Reinartz, "QST" **9,** 9 (April, 1925).

[13] Taylor, Proc. Inst. Radio Eng. **13,** 677 (December, 1925).

[14] Appleton, Proc. Phys. Soc. London **37,** Part 2, p. 22D (February, 1925).

[15] Nichols and Schelleng, Bell System Techn. J. **4,** 215 (April, 1925).

DATA FROM TAYLOR'S RANGE CHART

The observational data of interest in the present development are to be found in Taylor's Range Chart,[13] which presents in graphical form a summary of a large number of experimental observations on the transmission of radio waves of wave-lengths from 16 to 3000 meters over distances up to 10,000 miles. The experiments have been carried out during recent years by the Radio Division of this laboratory with the assistance of the American Radio Relay League and their coworkers in the foreign countries. On the chart, which is not reproduced here, are plotted the relative ranges of transmission of the various wave-lengths, as far as they have been investigated, reduced to a uniform condition, namely, 5 kilowatts in a normal transmitting antenna. The average ranges for day and night and for summer and winter are included.

From the chart certain new facts regarding the behavior of the short waves stand out. It has been found that for wave-lengths shorter than 50 meters the intensity of the received signal decreased as the distance from the transmitter was increased, reaching a value too small to be observed at a distance of a hundred miles or so. With further increase of distance the received signal remained undetectable until a region was reached where the received signal became strong again, rising rapidly to a maximum and thereafter decreasing rather slowly. The distance from the transmitter to the far edge of the region of silence, which we may call the "skip distance," was found to increase rapidly as the wave-length decreased; for a specified wave-length it was longer at night than in the day and longer in winter than in summer. The skip zone was not very sharply defined of course, but passed into the region of steady signals through a transition zone, sometimes called the "flicker" zone, where the signals were erratic and subject to violent fading. It may be emphasized that the skip zone was not merely a zone of uncertain signal reception, but a region where the signals were entirely absent for the most part; a conservative estimate would be that the intensity of the signal at a point three fourths of the distance out into the skip zone was at least 10^{-4} of the intensity of the signal zone beyond. The skip distances, denoted by $2s$, averaged throughout a year, for full daylight conditions, for wave-lengths 16, 21, 32 and 40 meters were 1300, 700, 400 and 175 miles, respectively. These are plotted as rectangles in Fig. 1. The values naturally can not claim great accuracy and may perhaps be in error by as much as a hundred miles. The skip distances at night are not yet known with precision. This is due perhaps to an insufficiency of data, but more probably to the fact that conditions at night are so erratic that even more extended observations would fix the distances only within wide limits. Present information indicates, however, that the night skip distances are on a rough average three or four times the corresponding day values.

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* A preliminary abstract of the present paper appeared in Science, p. 183 (August 12, 1925).

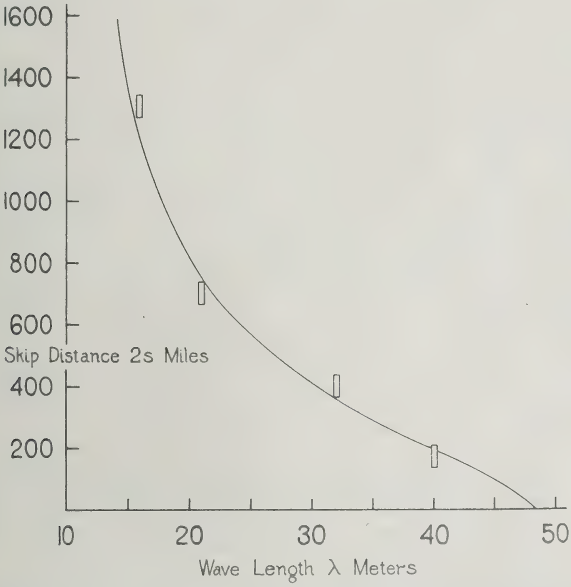

Fig. 1. The skip distances averaged throughout a year, for full daylight conditions, as a function of wave-length.

We regard these skip distance phenomena as demonstrating forcibly that two portions of the transmitted wave may be differentiated, one which clings to the earth and decreases rapidly in intensity until it is lost, and the other which moves in an upward direction and returns to the earth after refraction, with little attenuation in the Kennelly-Heaviside layer.

In Fig. 2 are plotted the ranges, under full daylight conditions, averaged throughout a year for uniform transmitting conditions, i. e. 5 kilowatts in a normal transmitting antenna, against the corresponding wave-lengths. Although the physical basis of the curve is essentially composite, for each wave-length may be propagated in a characteristic manner, the pronounced minimum in the curve at about 200 meters is taken to suggest a critical region of dispersion or of absorption. The agreement of the position of the minimum with the calculated critical wave-length 214 meters (§6) gives reality to this suggestion.

Dispersion Equations of a Magnetized Electron Gas

3. It is assumed that the regions of the Kennelly-Heaviside layer owe in the main their optical properties to the presence of the free electrons, and in the equations the influence of the magnetic field of the earth is taken into account. We follow the classical electron theory of Lorentz,[16] and in application to the present problem we assume no restoring force on the electrons due to the medium, no absorption, and no effect of the electrons on each other; this amounts to placing a, f and g equal to zero in equations (198) (see Lorentz, loc. cit.,[16] p. 139). Let ξ and E_x be the X components of the displacement of the electron from its equilibrium position and the electric force, respectively, and η, ζ, E_y and E_z the Y and Z components of the quantities. The charge on the electron is denoted by e, its mass by m; N is the number of

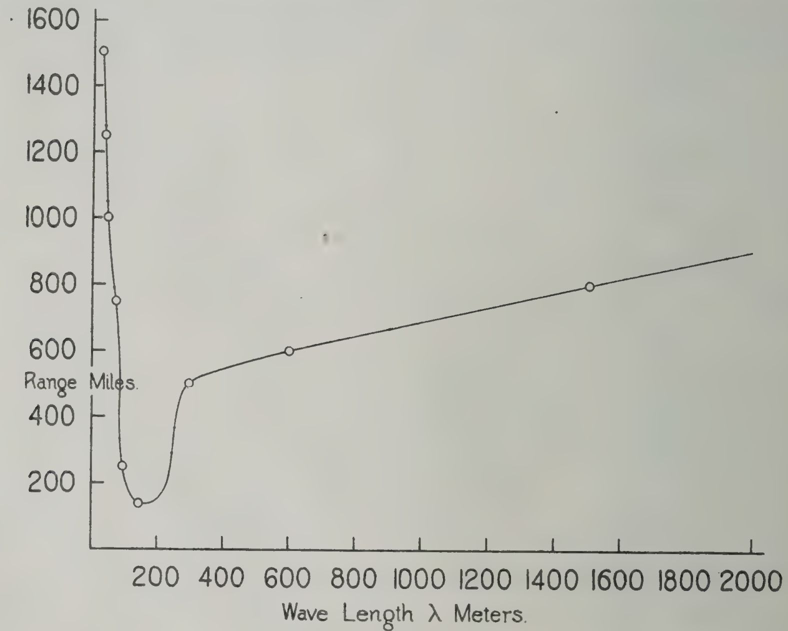

Fig. 2. The ranges, under full daylight conditions, averaged throughout a year, for uniform transmitting conditions, as a function of wave-length.

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[16] H. A. Lorentz, "The Theory of Electrons," Chapter IV (1916).

electrons per unit volume. The magnetic permeability of the medium is taken to be unity. All quantities are expressed in c.g.s., e.m. units.

4. *Propagation parallel to the magnetic field.* This case will apply approximately to North and South propagation. We denote the magnetic field by H and suppose it to have the direction of the axis of Z, which is also the direction of the propagation of the radiation. We take the radiation to be initially plane polarized. In Newtonian notation the equations of motion of the electrons are

$$\left.\begin{aligned} m\ddot{\xi} &= eE_x + He\dot{\eta}\,, \\ m\ddot{\eta} &= eE_y - He\dot{\xi}\,, \\ m\ddot{\zeta} &= eE_z\,. \end{aligned}\right\} \tag{1}$$

Let ϵ be the base of natural logarithms, and let all dependent variables of (1) contain the time only in the factor $\epsilon^{i2\pi tc/\lambda}$ where c/λ is the frequency, c is the velocity of light in vacuum, and i is $\sqrt{-1}$. The solution of (1) yields two vibrations circularly polarized in opposite directions, whose refractive indices μ are given by the relations

$$\mu^2 = 1 - \frac{C\lambda^2}{1-\lambda/\lambda_0}\,, \tag{2}$$

$$\mu^2 = 1 - \frac{C\lambda^2}{1+\lambda/\lambda_0}\,, \tag{3}$$

where

$$C = Ne^2/\pi m \quad \text{and} \quad \lambda_0 = 2\pi cm/He\,. \tag{4}$$

The details of this solution are here omitted for they are essentially the same as those given by Lorentz. If the refraction is not great or the distance of propagation is small the wave remains coherent and the two circularly polarized components add to give in general an elliptically polarized wave. For equal intensities of the two components the resultant wave is plane polarized with the plane of polarization rotated from its original direction. If the two components are separated, by greater refraction or distance, each will proceed as a circularly polarized wave.

5. *Propagation perpendicular to the magnetic field.* In this case, which will refer approximately to East and West propagation, the initially plane-polarized wave is resolved in general into two component vibrations with electric vectors parallel and perpendicular to H, respectively. The solutions of the appropriate equations of motion of the electron

yield refractive indices μ for the parallel and perpendicular cases, respectively,

$$\mu^2=1-C\lambda^2\,, \tag{5}$$

$$\mu^2=1-\frac{C\lambda^2}{1-\lambda^2/\lambda_0{}^2(1-C\lambda^2)}. \tag{6}$$

If the wave remains coherent the two plane vibrations unite to produce in general an elliptically polarized wave, but if the two components are separated, each will proceed as a plane polarized wave. Eq. (5) of course represents the propagation in the absence of a magnetic field as discussed by Larmor. It may be mentioned in passing, although no use is made of the fact here, that for the plane polarized wave component of formula (6) the electrons describe ellipses whose planes are parallel to the direction of propagation of the wave and perpendicular to H. From one point of view these vibrations can not be said to be transversal. This peculiar instance was recognized long ago by Voigt. The case may be compared with the motion of the particles on the surface of deep sea waves on water.

6. In the general case of propagation at an angle with the magnetic field all four of the modes of vibration just discussed may occur in greater or less proportion, with the result that the wave, if coherent, will become elliptically polarized, the orientation of the axes and the eccentricity of the ellipse changing as the wave proceeds. If the refraction or distance of propagation is sufficiently great the various components may be separated from each other.

Taking the value of H for the earth's magnetic field to be 0.5 gauss, λ_0 from (4) comes out to be 214 meters. This is the value calculated by Nichols and Schelleng (loc. cit.) and is the value used for λ_0 throughout this paper. The minimum at about 200 meters of the curve of Fig. 2 agrees closely with $\lambda_0=214$ meters. This is regarded as an experimental confirmation, indirect of course, of the theoretical calculation.

To bring out the characters of the various dispersion formulas the curves 2, 3, 5 and 6 have been plotted in Fig. 3 from Eqs. (2), (3), (5) and (6) respectively, choosing $N=3.95\times10^5$ electrons per cc. In the region of wave-lengths less than 50 meters the curves do not differ greatly. With increase in λ all the curves of Fig. 3 descend to zero and μ becomes imaginary, remaining so for the longer waves in the case of curves 3 and 5. For curves 2 and 6 μ remains imaginary until wave-lengths λ_0 and $\lambda_0\sqrt{1-C\lambda^2}$ are reached, respectively. At these wave-lengths, called the "critical" wave-lengths, μ is $\sqrt{\pm\infty}$ and as λ is increased beyond them μ descends from high positive values finally to low values again. As a matter of fact the critical wave-length $\lambda_0\sqrt{1-C\lambda^2}$ appears to be of no physical importance, for, due to the presence of C in this expression, no wave can reach the region of electron density where this critical condition for the wave prevails.

7. *Absorption in the Kennelly-Heaviside layer.* Among various possible causes of absorption of energy from the electromagnetic wave by the upper reaches of the atmosphere the most important would seem to arise from collisions between electrons and molecules. This would convert a portion of the energy of the wave into heat. Simple calculations, such as given by Larmor and by Nichols and Schelleng, indicate that the probability of collision is small, so that absorption due to this cause is negligible, except in the region near the critical wave-length λ_0 and for very long waves outside of the usual radio range, which have a very slow oscillation. In lower regions of the atmosphere, where the density of molecules is greater, absorption due to collision might exist even for shorter waves. If we assume that this type of absorption can be

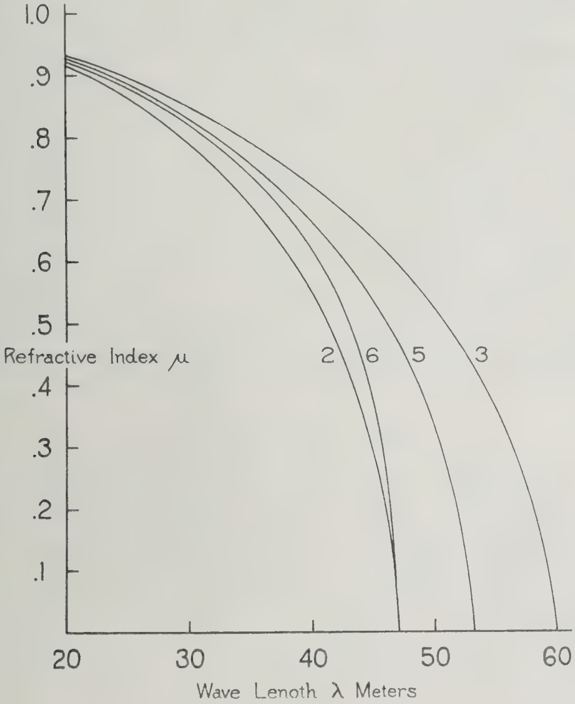

Fig. 3. Refractive indices of the Kennelly-Heaviside layer as a function of wave-length for rays in and perpendicular to the direction of the earth's magnetic field (Eqs. (2), (3), (5), (6)).

expressed as a frictional term in the equations of motion of the electron, which is no doubt permissible within limits, the dispersion formulas are all available in treatises on magneto-optics. For small absorption these differ from Eqs. (2), (3), (5) and (6) by wholly inappreciable amounts for wave-lengths removed by, say, 30 meters from $\lambda_0 = 214$ meters. Near to this critical region the absorption term produces complex modifications, which have been discussed by Nichols and Schelleng. It is, however, justifiable to neglect absorption as long as the critical region is avoided; and we have been content to avoid this region because of its complexity and because the observations on these wave-lengths are mainly qualitative.

For a wave traveling near the earth the matter of absorption is quite different. This has been discussed by Zenneck,[17] Sommerfeld and others who showed that the earth absorption may become very high for the shorter waves. The successful radio transmission to distances as great as half-way around the earth with waves below 90 meters proves that the attenuation is small, no matter to what cause it is attributed, and this combined with the pronounced earth absorption for the shorter waves leads forcibly to the conclusion that the waves must travel in the upper atmosphere and that the absorption in these regions is slight.

Reflection Theory

8. It is assumed that the lower levels of the atmosphere of the earth are relatively free from electrons and that the lower surface of the Kennelley-Heaviside layer, the region of relatively great electron density, is sharply marked. A radio ray transmitted in an upward direction would travel in a straight line and after reflection from the layer would return in a straight line to the earth. Actually, of course, the optical constants of the lower atmosphere merge without discontinuity into those of the electronic regions, so that a ray instead of being sharply reflected is refracted along a curved path. As often happens in theoretical physics, we consider first the simple case of sharp reflection and then pass to a refraction theory which is probably more in accord with the real state of things. Moreover, many of the conclusions of the reflection theory are found to be unchanged for the refraction theory.

We take the lower boundary of the layer, represented by AE in Fig. 4, to be a spherical surface parallel to the surface of the earth and at a height h above the earth. The radius of the earth is R. Let CAF

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[17] Zenneck, "Wireless Telegraphy," 3rd Ed., p. 248 (1915).

be the path of a radio ray transmitted from C which is reflected from A at an angle ϕ and let the length of the arc CF be $2s$; s subtends the angle θ at the center of the earth. *It is now assumed that when $2s$ is the observed skip distance for a specified wave-length ϕ is the critical, or Snell, angle of total reflection of the wave from the layer.* Since the refractive index of the atmosphere below the layer is unity this assumption of course involves the condition that the refractive index of the layer is less than unity for those wave-lengths for which a skip distance exists. Otherwise a critical angle of total internal reflection would be impossible and no skip zone would exist. If μ is the refractive index of the Kennelly-Heaviside layer, then from Snell's Law,

$$\mu = \sin \phi \ . \tag{7}$$

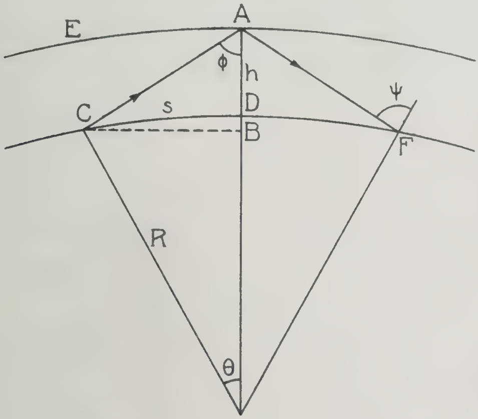

Fig. 4. Reflection from the Kennelly-Heaviside layer.

From the geometry of Fig. 4,

$$\sin \phi = CB/AC = R \sin \theta / \{ R^2 \sin^2 \theta + (R+h-R \cos \theta)^2 \}^{1/2} \tag{8}$$

and

$$s = R\theta \ .$$

The discussion is limited for the moment to the special case of dispersion represented by Eq. (2). When this equation was combined with (7) and (8) to eliminate ϕ and θ there resulted a relation between the unknown quantities h and C, the known constants R and λ_0, and the observed quantities λ and s. The substitution of the observed skip distances $2s$ for wave-lengths 16 and 40 meters into this relation yielded two equations in h and C. Eliminating C from these led to a quartic equation in h, which determined h and thence C. with these values of h and C, with $R=3970$ miles and with $\lambda_0=214$ meters the $2s,\lambda$ curve was plotted and readjusted to approximate a least square solution.

The final $2s,\lambda$ curve is shown in Fig. 1, and the values of h and C corresponding to this curve were 152 miles and 3.54×10^{-8}, respectively. With this value of C in (4) together with the usual values of the electronic mass and charge, N came out to be 3.95×10^{5}. The agreement between the theoretical curve and the observed values in Fig. 1 is regarded as a confirmation of the correctness of the theory. Further, the values of h and N which have emerged appear reasonable. h is well within the aurora domain which, according to Stormer[18] is between 50 and 300 miles above the earth. In this region where the pressure may be of the order of 10^{-5} atmospheres a simple calculation indicated that an electronic density of the order of 10^{5} per cc. is easily possible, the electrons supposedly being caused mainly by the ultraviolet light of the sun. The values for N and h appeared to be quite definitely established as far as the present theory and calculations were concerned, for a variation in them of as little as 20 percent gave rise to discrepancies between the calculated and observed skip distances. Further, N and h did not depend at all critically on the value chosen for λ_0, changing, for example, by only a few percent when λ_0 was varied from 120 to 300 meters. The reason for this lay in the nature of the dispersion equation (2), and the fact that the wave-lengths below 60 meters were remote from the critical wave-length λ_0. It would therefore appear that N and h and the refraction of the rays are little influenced by time or space variations in the earth's magnetic field.

9. The dispersion curve, μ against λ, plotted from Eq. (2) with $\lambda_0=214$ meters and $N=3.95\times10^{4}$, is shown by curve 2, Fig. 3. The Snell angles ϕ calculated by means of (7) for wave-lengths 16, 21, 26, 32 and 40 meters were 71.8, 65.2, 58.4, 49.2 and 33.4 degrees, respectively. The angles which the direction of the down-coming wave at the edge of the skip zone makes with the vertical are for the respective wave-lengths 79.5, 70.6, 62.1, 51.8 and 34.8 degrees. These were calculated from the relation $\psi=\phi+\theta$ (see Fig. 4). An experimental determination of these angles would offer direct evidence concerning the present theory. In such experiments complicating effects of the ground at the receiving station should be avoided or recognized.

Since h is roughly proportional to s, the fact that the night skip distances are about three times the day values indicates that h at night is three times the day value. The angles ψ will be greater at night than in the day by amounts corresponding to the change in θ.

10. Because of the bulge of the earth and the curvature of the layer, the curve of Fig. 1 ceased to exist at wave-length 14 meters. The

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[18] Stormer, Proc. Phys. Soc. London, **37**, part 2, 50 D (1925).

Snell angles for wave-lengths shorter than this being so nearly 90° that even rays transmitted horizontally from the surface of the earth could not be totally reflected from the layer. Since it appears that the overhead reflected (or refracted) wave and not the ground wave is all-important in long-distance short wave radio transmission, *the present theory indicates that communication over long distances by means of wave-lengths less than 14 meters will be relatively difficult.* This is due to the mechanism of the propagation entirely apart from the inherent technical difficulties in the apparatus for producing these very short waves with appreciable intensity. The few experiments which have been made in this region support this conclusion; for example, no long distances have been reached in the case of tests with 5 meter waves. It is hardly necessary to remark that due to unusual ultra-atmospheric conditions, etc., long distance communication with very short waves may be successful at times. Such cases should prove to be the exception rather than the rule.

11. The foregoing calculations have been based on dispersion equation (2) which refers to one of the circularly polarized waves arising from propagation along the magnetic field. They are, furthermore, valid and accurate, within limits, for the general case of propagation of a wave with electric vector at a random and changing angle to the magnetic field, because the general case differs but slightly from the special case in the region of wave-lengths below 40 meters. This is evident when the μ,λ curves for the various dispersion equations, Eqs. (2), (3), (5) and (6), are compared. These are plotted in Fig. 3, curves 2, 3, 5, and 6 respectively, using the constants $\lambda_0 = 214$ meters and $N = 3.95 \times 10^5$ or $C = 3.54 \times 10^{-8}$. For wave-lengths below 40 meters the refractive indices for the various curves are closely the same, and hence the Snell angles and the skip distances are approximately the same. In this connection curve 3 may be disregarded for it refers to one of the component waves of propagation parallel to the magnetic field and wherever this exists the other component represented by curve 2 also must exist. The skip distances from curve 2 are all less than those from curve 3 and are therefore the ones which would be observed. The cases of propagation which differ most widely are, then, those represented by curves 2 and 5. These yield skip distances which differ by about 60 miles, those from curve 5 being the greater. If Eq. (5) instead of (2) had been used h and N would have come out roughly 10 percent different from the values for (2). Therefore the values of h and N, which have been determined from curve 2, may be considered to be sufficiently accurate for the general case, which lies

somewhere between the conditions of the curves 2 and 5; especially so, since the values can only be looked upon as rough averages of quantities which probably vary each moment of the day throughout the year. It follows at once from the approximate sameness of curves 5 and 6 which refer roughly to East and West propagation, and of curve 2, which refers to North and South propagation, that the skip distances do not vary appreciably with the compass direction of propagation. This is in accord with the experimental observations.

In the band of wave-lengths between 50 and 60 meters the curves of Fig. 3 suggest an appreciable variation in skip distance with the mode of propagation. For example, if the conditions of curve 3 obtained, we might expect a skip distance of 120 miles for a 50 meter wave, whereas under the conditions of curve 2 no skip distance would exist. There is some evidence that this effect exists although the observations are none too certain because of the ground wave which may fill in the skip region. However, there is noticed at times an unusual flickering in the intensity of signals in this region which farther away are stronger and steadier.

12. Up to this point we have mentioned only the contribution of the electrons to the dispersion in the upper atmosphere, and we may now show that the more massive ions have little influence. In the dispersion formulas (2), (3), (5) and (6) the effect of the ions on μ may be calculated to a first approximation by adding another term (or terms, there being a term for each type of ion) similar to the last term of each equation, using the mass of the ion instead of the electron, which for, say, a nitrogen ion is 10^4 greater. The quantity $C=Ne^2/\pi m$ in the numerator of the ionic term is then 10^{-4} of the corresponding quantity for the electronic term for the same density of ions and electrons, the denominators being approximately the same for short waves. Therefore the ionic term will be negligibly small compared to the electronic term, except for very long waves outside of the usual radio range unless there are at least 10^3 as many ions as electrons. Such a preponderance of ions is hardly to be expected in general. In view of this and of the good agreement of the theory with the observations, as indicated in Fig. 1, the conclusion may be emphasized that *the reflection (or refraction) of radio waves in the layer is caused in general by the electrons and not by the more massive ions.* This may be regarded as a definite proof of the presence of considerable numbers of electrons in the upper atmosphere of the earth.

REFRACTION THEORY

13. The physical conditions in the upper atmosphere are scarcely such as to render tenable a theory of reflection, for the transition from

the low electron density of the lower atmosphere to the higher concentration of electrons in the Kennelly-Heaviside layer must be gradual and not abrupt. We therefore pass to a theory of refraction as offering a more exact picture of actual conditions, with the preliminary remark that the results of the refraction theory are for the most part identical with those of the reflection theory. This is to be expected since reflection is only a special case of refraction. We must now call attention to a circumstance which throws further doubt on a reflection theory and which supports a refraction theory. If we suppose, as has been done, that the edge of the skip zone marks the Snell angle of total reflection then, as we pass into the skip zone to points where reflection occurs at angles less than the critical angle, the reflected intensity will become less, but will not drop to zero, and in the case of rather oblique incidence, as with the 16 meter wave, the reflected intensity may be decreased by only a few percent. It would therefore follow that the intensity of the signals would drop off very slowly as the skip zone was entered never reaching low values except at nearly normal incidence, and even there not zero. It is well known, on the contrary, that the signal intensity at, say, a distance of one fourth of the way in from the outer edge of the skip zone, is less than 10^{-4} of the intensity in the region beyond the skip zone. This discrepancy in the case of the reflection theory does not occur for the refraction theory.

The calculations become much simpler if we consider the case of a flat earth instead of the curved earth discussed heretofore. For a flat earth Eq. (8) of the reflection theory becomes

$$s = h \tan \phi \tag{9}$$

which is of course a close approximation to (8) for short distances, up to 1000 miles. It will be shown later, however, that entirely apart from this approximation, the flat earth calculation can be referred to a curved earth with exactness.

The elaboration of a refraction theory requires the determination of the ray-paths of the wave, and these may not be determined explicitly without a knowledge of the variation of the optical constants of the atmosphere with the distance above the earth. The method of procedure has thereupon consisted in assuming a number of types of this variation and in investigating the results of these assumptions.

14. It is assumed that the surface of the earth is flat and that the refractive index μ of the region lying above the earth is a function of y and not of x, where Y and X are the coordinate axes in the vertical and horizontal directions, respectively. μ is assumed finite, single-valued and continuous for a specified wave throughout the region. Let ABC,

Fig. 5, be the ray which is projected from a point A on the surface of the earth at an angle ϕ with the vertical let μ_0 be the refractive index of the atmosphere at A. Let adjacent elements on either side of a point B on the curve make angles i and $i+di$ with the vertical, and let the refractive indices at these elements be μ and $\mu+d\mu$, respectively. Then, from Snell's Law

$$(\mu+d\mu)/\mu=(\sin i)/\sin(i+di).$$

Whence

$$\mu=a/\sin i\,,$$

where a is a constant of integration. From the initial conditions $\mu=\mu_0$, $i=\phi$, we obtain

$$a=\mu_0 \sin\phi \tag{10}$$

and

$$\mu=(\mu_0 \sin\phi)/\sin i \tag{11}$$

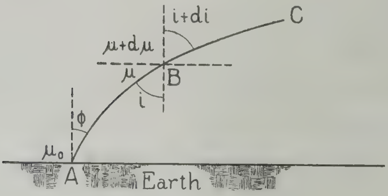

Fig. 5. Refraction of a radio ray in an electron atmosphere of variable density.

This is Snell's Law generalized for the present problem. Since (11) must be satisfied at every point of the ray-path, the differential equation of the path is

$$dy/dx=-\cot i=-\sqrt{(\mu^2-a^2)/a^2} \tag{12}$$

where $\mu=f(y)$ and a is independent of x and y. This may not be integrated explicitly and therefore the equation of the ray-path can not be determined, unless $\mu=f(y)$ is known. In order to proceed farther various assumptions as to $f(y)$ are made and investigated in the following paragraphs.

15. *Case 1. Electron density proportional to height.* It is assumed that the electron density sets in at the surface of the earth and increases proportionally with the height above the earth. We write

$$N=\beta y \tag{13}$$

where N is the electron density at a point y cm above the surface of the earth. Then, from (3) for each of the dispersion formulas (2), (3), (5), and (6),

$$\mu^2=1-\gamma y \tag{14}$$

where γ is determined by identifying (14) with each dispersion formula in turn. At the surface of the earth $y=0$ and from (14) $\mu=1$. Therefore, from (10)

$$a=\sin\phi. \tag{15}$$

Introducing (14) into (12) and integrating gives for the equation of the ray-path,

$$x^2=\{4a^2(1-a^2-\gamma y)\}/\gamma^2. \tag{16}$$

This is a parabola. The constant of integration has been eliminated by a shift of the curve along the X axis. The maximum height h above the earth reached by the ray is

$$h=(1-a^2)/\gamma. \tag{17}$$

The ray comes down to the earth again at a distance $2x_0$ from its starting point, where

$$x_0=2a\sqrt{1-a^2}/\gamma\ . \tag{18}$$

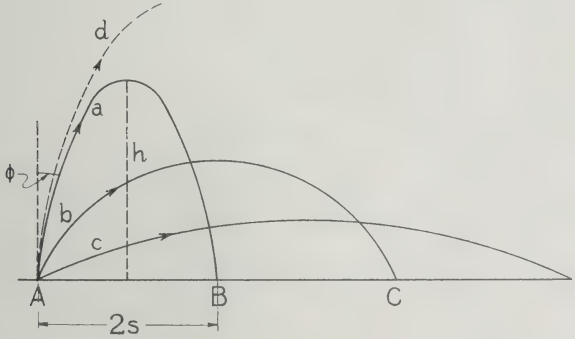

Fig. 6. Refraction of radio rays transmitted from A at varying angles through an electronic atmosphere whose density is proportional to the height.

Combining (18) with (15) and (17) leads to

$$x_0=2h\tan\phi\ . \tag{19}$$

The ray-paths plotted from (16) for a specified wave transmitted from A, Fig. 6, at increasing angles ϕ are illustrated by curves a, b, and c, Fig. 6. It is seen that as ϕ increases h decreases and $2x_0$ increases. *We may now identify AB, the distance between the feet of curve a, as the skip distance for the wave in question.* This means that any other ray such as d, whose angle of projection ϕ is less than that of ray a, will not return to the earth between points A and B; it may possibly return at some distant point or perhaps not at all. It follows, therefore, that the law of electron distribution given by (13) ceases to hold above the summit of curve a. Just what will be the law above h is of course unknown, but this much can be said, that the electron density must increase less rapidly above h than it did below h. *Therefore the "height of the Kennelly-Heaviside layer" means merely the distance above the earth to the region where the rate of increase in the electron density with the height becomes less. And because of its physical appeal, in spite of other mathematical possibilities, we take this region to be the region of maximum electron density.*

According to the supposition just made that AB of curve a, Fig. 6, be the skip distance for the wave, formula (19) becomes

$$s=2h\tan\phi\,. \tag{20}$$

We might now introduce the observed skip distances into (20) and from the relation $\mu=\sin\phi$ at the height h and one of the dispersion equations determine h and N, just as was done in the case of reflection. It is not necessary to do this, however, because of the similarity of (20) and (9). It is seen that these formulas, which refer to a flat earth, are the same except that h of (20) is one-half h of (9). We may therefore conclude that if the skip distance refraction formula for a curved earth corresponding to (20) had been developed, it would be nearly the same as (8) which is the reflection formula for a curved earth corresponding to (9). This is true because only matters of geometry enter into the transformation from a curved to a flat earth. We may finally conclude that *all the numerical facts of this refraction case are exactly the same as those which have been derived from the reflection theory, except that h is one-half the h of the reflection theory.* h is now 76 miles, but N, the calculated $2s,\lambda$ curve, the angles at which the rays at the edge of the skip zone descend to the earth, etc., are as before.

We may now emphasize the contention stated in §13, which pointed out that within the skip zone the intensity of the received signal is known to be 10^{-4} or less of the intensity in the surrounding signal zone. The refraction theory is in accord with this, for referring to Fig. 6, there is no ray-path possible which connects the transmitter A with a receiver inside the skip zone.

16. *Case 1a.* The assumption of (13) and the result that for $y=76$ miles $N=3.95\times10^5$ electrons per cc is scarcely possible, for this would mean that at a height one mile above the earth there are 5×10^3 electrons per cc which is probably too large a number in general. If we then suppose that there are no electrons in the lower atmosphere up to a height h_0 and that the linear density law (13) sets in thereafter, it is easily seen that the ray-paths are straight lines in the region h_0, changing to arcs of parabolas in the region above h_0 and finally be-

coming straight lines again when the ray returns to levels below h_0. The skip distance formula corresponding to (20) is in this case

$$s=(h_0+2h')\tan\phi \cdot \tag{21}$$

$h'+h_0$ is the height of the summit of the ray above the earth, which is the height of the Heaviside layer. As h_0 increases from 0 to 76 miles, $h'+h_0$ increases from 76 to 152 miles, and we pass from the electron distribution of (13) to the case of abrupt reflection. Because of the similarity of (21) and (20) all that has been said of the applicability of the reflection theory results to Case 1 applies equally well to the present case of refraction.

17. *Case 2. Electron density proportional to square of height.* In the notation of Case 1, it is assumed that

$$N=\beta y^2\,. \tag{22}$$

Proceeding exactly as in Case 1, the equation of the ray path is

$$y=(\sqrt{1-\alpha^2}/\sqrt{\gamma})\sin(x\sqrt{\gamma}/\alpha)\,, \tag{23}$$

which is a sine curve. The skip distance formula is

$$s=(\pi h/2)\tan\phi\,, \tag{24}$$

and the height h comes out to be 97 miles.

18. *Case 3. Electron density proportional to exp. (height).* It is assumed that

$$N=\beta\epsilon^y \tag{25}$$

and proceeding as before the equation of the ray-path is

$$x=\frac{\alpha}{\sqrt{1-\alpha^2}}\log_\epsilon\left\{\frac{2(1-\alpha^2)-\gamma\epsilon^y+2\sqrt{(1-\alpha^2)(1-\gamma\epsilon^y-\alpha^2)}}{\gamma\epsilon^y}\right\}. \tag{26}$$

The skip distance formula is

$$s=(\tan\phi)\log_\epsilon\left\{2\epsilon^h-1+2\sqrt{(\epsilon^h-1)\epsilon^h}\right\}, \tag{27}$$

from which h is 149 miles. This is a special case of an exponential distribution, but possesses all the essential features of a more general type which would be described by $N=\beta e^{by}$, where b is a constant.

Since the skip distance formulas (24) and (27) are similar to (9), the reflection theory results also apply to these cases, the height of the Heaviside layer being different, of course. Furthermore, corollary cases similar to Case 1a when carried out for Cases 2 and 3 gave results exactly similar to those of Case 1a. This is so evident that the details are omitted.

19. *Case 4. Electron density proportional to square root of the height.* From the assumption that

$$N=\beta y^{1/2} \tag{28}$$

the equation of the ray-path is

$$x=(4\alpha/\gamma^2)\sqrt{1-\gamma y^{1/2}}\{1+2\alpha^2/3+(1-\gamma y^{1/2})/3\}\ . \tag{29}$$

The skip distance formula is

$$s=(8/3)h\tan\phi\cdot(3/\cos^2\phi-1)\ . \tag{30}$$

It was found impossible to choose constants for the dispersion formulas such that (30) be in accord with the observed skip distances. Similar discrepancies with observation resulted from the assumption that $N=\beta y^{1/3}$ and $N=\beta y^{1/4}$.

20. *Case 4a.* In this instance we modify Case 4, just as was done in Case 1a, and assume that no electrons exist below a height h_0 and that the electron distribution of Case 4 begins there. The skip distance formula becomes

$$s=h_0\tan\phi+(8/3)h'\tan\phi\cdot(3/\cos^2\phi-1)\ . \tag{31}$$

It was found that this formula was at variance with the observed skip distances as long as the second term was important, which occurred when h_0 was small. As h_0 becomes larger the second term becomes of less effect, and we appoach the sharp reflection case and better agreement with observation.

21. In taking up the refraction cases 1, 2, and 3 in turn we have passed from an electron distribution linear with the height progressively to electron distributions for which the N, y curve becomes more and more convex to the Y axis, approaching the distribution for sharp reflection, and have arrived at heights of the Heaviside layer which became in turn nearer to 152 miles. All these have yielded the same $\lambda,2s$ curve in agreement with observation, i. e., the curve of Fig. 1, and therefore all are equally possible as far as this agreement is concerned. On the other hand, it has been shown in Case 4 that an electron distribution for which the N,y curve is concave to the Y axis led to pronounced discrepancies with the observed skip distances. This is all in comforting agreement with reasonable expectation. On general physical grounds one would expect an electron distribution whose rate of increase became greater with the height, whereas it is difficult to imagine the stable existence of a distribution whose rate of increase became less with the height. The conclusion to be derived is *that the electron density N,*

during full daylight and averaged over all the days of the year, of the atmosphere of the earth increases with the height y in such a way that the N,y curve is for the most part convex to the Y axis, and that N reaches a maximum value of the order 10^5 *for a height which is between 70 and 150 miles.*

Again, the increase of the skip distance at night which indicates an increase in h is to be expected. For, with the removal of the sun's radiation, (electromagnetic, electronic, etc.), which is probably the most potent cause of ionization in the atmosphere, recombination of the ions and electrons will occur. The electron density therefore becomes less and the radio rays must search higher altitudes before being turned back to the earth.

22. Certain details of the dispersion equations (2), (3), (5) and (6) are of interest. From all the equations at any wave-length less than $\lambda_0 = 214$ meters, μ decreases to zero and becomes imaginary as N (or C) increases. This means that a ray of this wave-length directed normally upwards passes through regions of decreasing μ (and hence moves with increasing velocity) until it reaches that electron concentration for which $\mu = 0$ and there is totally reflected (or refracted) back to the earth. *Therefore wave-lengths from about 60 to 200 meters will be totally reflected from the layer at all angles of incidence.* The different component modes of polarization will penetrate to different heights. For waves shorter than 50 meters, N can not become large enough to make μ imaginary, since the calculations fix the maximum value of N as 10^5, and hence these rays are not totally reflected at normal incidence, but at a greater angle; this of course is the essence of the fore-going skip distance theory.

For waves longer than 214 meters, μ decreases to zero and thence to imaginary values with increase of N in the cases of equations (3), (5) and (6). From Eq. (2) however, μ is always positive for these waves and increases from 1 as N grows larger. *Therefore for waves longer than 214 meters the modes of polarization corresponding to equations* (3) (5) *and* (6) *will be totally reflected from the layer at all angles of incidence, the mode of equation* (2), *however, always being refracted upward and being probably lost.* (Eq. (5) has further mathematical complexities which appear to be of no physical significance). The prediction that these waves suffer total reflection even at normal incidence should perhaps admit of direct experimental proof. For long waves, greater than 500 meters, (3) reduces approximately to $\mu^2 = 1 - C\lambda\lambda_0$ and (5) and (6) to $\mu^2 = 1 - C\lambda^2$. These are about the same for small values of C, and the latter is the refraction formula for zero magnetic field. Hence the earth's magnetic field has little influence in the bending of the long waves, and therefore Larmor's development, which neglected the magnetic field of the earth and referred to long waves is valid throughout.

Distortion of the Received Wave

23. We must now call to mind certain well-known radio phenomena concerning the distortion of the received wave usually resulting in fading, i. e., fluctuations in intensity, of continuous wave signals and in poor modulation and fading of speech signals. Two general types of fading are differentiated, which we now recognize as attributable to quite different causes. One type, which is common to all wave-lengths is an intensity fluctuation of relatively long period, of the order of a second or more. This is usually more noticeable at nearer distances than at greater distances from transmitter, and in general the longer the wave the slower the fluctuation. The other type is a fading at high speed, the signal intensity often varying from full strength to practically zero at a low audio frequency of the order of, say, 100 oscillations per second. This appears as a change in the quality of the heterodyne note when continuous wave signals are being received and as bad distortion in the case of speech signals. The audio frequency fading characteristic applies only to certain bands of wave-lengths at certain distances from the transmitter; it is, generally speaking, less observable in the day time and at longer distances. More specifically, for waves longer than 800 meters, roughly, the high speed fading rarely occurs; in the broadcast band, 300 to 600 meters, it is noticeable only at intermediate distances, at night especially, from about 100 to 1000 miles from the transmitter. In the region of shorter wave-lengths from 60 to 120 meters the high speed fading is violent at night for distances from roughly 5 to 300 miles from the transmitter. For the wave-lengths 16 to 40 meters the audio frequency fading is found in the flicker zones at the edge of the skip regions. Every detail of these fading phenomena finds a ready explanation in terms of the refraction ideas of this paper, and although qualitative, furnishes strong confirmation of those ideas.

24. With regard to the fading at low frequency, of a few seconds in period, we adopt the view, already suggested by many others, that this is due to a distortion of the received wavefront by motions of large clouds of the refracting electron medium. On the assumption, which appears very reasonable, that the bodily motions of the electron clouds are of the same order of velocity and extent as the air movements and

currents in the lower atmosphere, one would expect low frequency fluctuations in a wave refracted through such a medium. The phenomenon is a repetition on a larger and slower scale of the twinkling of the stars or of the unsteadiness of a scene viewed over the surface of a hot road. For longer waves motions of larger electron clouds are necessary to modify the wave-front, and these on the average would be expected to be slower than in the case of smaller clouds, so that the fading would be slower. Futher, for long distances for all wave-lengths the integrated cloud movements and hence the refraction effects would be expected to average out. This is all in accord with observation.

25. The audio frequency fading is attributed to shifting interference patterns, and finds its optical analogue in the "light beats" of Airy and Righi.[19] Thus, considering the band of waves from 300 to 600 meters, which exhibit occasionally audio frequency fading at distances from 100 to 1000 miles from the transmitter, it is seen from §22 that the various polarization components of the wave, except that of Eq. (2) are totally reflected from the layer at all angles of incidence. Therefore, in this instance any receiver, no matter where situated, may expect to receive in general four possible rays, the ground wave and the three overhead waves of Eqs. (3), (5) and (6) which travel to the receiver by different paths. In the first 100 miles from the transmitter the ground wave is sufficiently intense to drown out any variations contributed by the overhead components. Beyond 100 miles the intensity of ground wave for these wave-lengths becomes comparable with or less than that of the overhead waves, with the result that a complicated interference pattern of various states of polarization and intensities is formed about the receiver. Movements of the electron layer will cause this pattern to shift to and fro, thereby causing the rapid fluctuation of signal intensity. In daylight the electrons gather into low lying clouds of relatively great density gradient, so that the paths of different overhead rays are relatively close together and the interference pattern becomes broad and hazy. Its movements therefore cause little change in the signals. At night, however, the electrons are more diffuse and their density gradient is much less, so that the ray paths are more wide'y separated. The interference bands are therefore narrower and sharper and the motion of the pattern will cause rapid and violent intensity variations. At distances greater than 1500 miles the ray paths are so long that the interference pattern becomes indistinct in both day and night and the average effects on it of electron cloud movements become less. It is interesting that these

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[19] Airy and Righi, Journal de Physique, **2**, 437 (1883).

considerations call for the propagation of even these relatively long waves to great distances by an overhead route.

By similar reasoning fast fluctuations would not be expected to occur for long waves at any place, because in the near distances the ground wave is strong and in the far distances the interference pattern is diffuse. In the case of the 16 to 40 meter band it is easily seen that the possibilities for sharp interference exist only on the edge of the skip zones.

26. The discussion of the wave band from 60 to 120 meters is along similar lines. Here, however, the rapid fading occurs at distances as small as 5 miles from the transmitter. This means that for these waves at this distance the over-head components reach the receiver with an intensity comparable with that of the ground wave, even after traveling 100 miles or so up into the upper atmosphere and being reflected back at nearly normal incidence! There seems to be no escape from the conclusion that the ground wave in this case dies out rapidly and that the over-head components are very perfectly reflected. Thus what has long been an exceedingly puzzling phenomenon finds an equally startling explanation, startling at least until one accepts these ideas.

27. The various components of the wave, besides interfering, also may arrive at a receiver at different times, because of the different paths which they traverse. This will have no effect on the interference patterns just discussed, if the wave trains are long, as in continuous wave signals, but will become an additional cause of distortion in the case of short wave trains, such as the modulated waves of speech signals. In order to estimate the magnitude of this we assume that the electron distribution of Case 1a is the one which actually exists for daylight conditions and take $h_0=30$ miles; $N=0$ at this height. From the skip distance data and Eq. (21), $h'=61$ miles and $h_0+h'=91$ miles where $N=3.95\times10^5$. This gives the electron density gradient. From this and the dispersion equations (2), (3), (5) and (6) it is found that $\mu=0$ at heights 69, 86, 78 and 64 miles, respectively. These are the heights where total reflection occurs for the respective waves, as discussed in §22. Assuming normal incidence the differences of the paths of the rays from the transmitter to the region of total reflection and back to the receiver are roughly 20 miles, or 10^{-4} seconds. The rays, moreover, pursue their respective paths with different speeds, which are slower in the longer paths. Calculation shows that this will increase the time differences of the paths by two or three times, making them, say, 3×10^{-4} seconds. This would perhaps be barely perceptible in speech signals. At night, however, the ray-path differences would be

increased roughly three times, and the time differences would be of the order of 10^{-3} seconds or more, which would cause strong distortion of the speech signals. This estimate of the time differences of the rays has depended on the electron distribution assumed for the calculation. This suggests that an experimental analysis of the distortion in signals of wave-lengths 60 to 120 meters received at short distances from the transmitter would perhaps lead to more definite information about the electron distribution.

LONG DISTANCE TRANSMISSION

27. In the light of the foregoing conclusions it is of interest to consider the character of the reception at various distances from the transmitter. No attempt to cover all details will be entered upon, but a few cases deserve remark. It is convenient to make the diagrams from the reflection theory; the conclusions from these will be the same as from a refraction theory. In Fig. 7 the curved line AL is the surface of the earth and BC' the Kennelly-Heaviside layer at a height of 150 miles. Suppose that the radio rays from the transmitter A are confined to the space BAC. The upper limiting ray AB descends to F, where AF is the first skip region, is reflected back to D, down again to the earth at H, etc., continuing around by successive reflections. The lower limiting ray may be tangent to the earth as shown by AC' or may be inclined at an angle to the horizontal in the manner of AC. In the latter case if $AG<AH$, where $AH=2AF$, there exists a second smaller skip region GH. From a continuation of the drawing further skip zones are found at greater distances. These are possible, but perhaps not probable because they become successively smaller and more ill-defined.

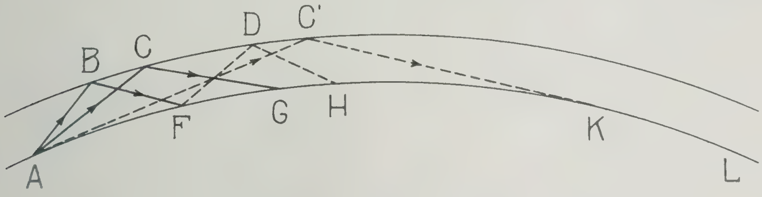

Fig. 7. Paths taken by radio rays in traveling around the earth.

If the bundle of transmitted rays is limited on its lower side by the tangent ray AC', which is reflected to the earth again at K, the region KL can be reached by a ray from A only after at least one ground reflection and two layer reflections (refractions). With a layer height of 150 miles AK is 2000 miles. The region FK, on the other hand, can be reached by a ray which has experienced only one layer reflection and no ground reflection. Therefore, because the ground reflecting power may vary with the locality, one might expect possibilities of poorer signals in the region KL than in the region FK, quite apart from the difference in remoteness; or, more graphically, the poor reception at a station 5,000 miles away may be due to a forest 2500 miles away. This distinction between the regions less and greater than 2,000 miles would seem to be generally valid at all wave-lengths for which the direct ground wave is inoperative and for all the electronic distributions permissible in §§15 to 20.

The observational data relevant to these questions are none too certain, but a recent program of tests with the 25.6 meter transmitter from this station (NKF) has permitted a few conclusions. A portion of the program involved the reception of the signals at every hour of a 24-hour day by some forty stations scattered to 7000 miles distance. In the first place, the first daylight skip zone for 25.6 meters was found to be between 500 and 600 miles, which is in excellent agreement with Fig. 1. Secondly, no secondary skip zone, as GH, Fig. 7, appeared; the region from 700 to 1200 miles in daylight being unmistakably one of good signals. This meant merely that the lower transmitted rays were probably near to tangency with the earth, as AC', Fig. 7. In this connection it might be possible to elevate the ray AC' until the second skip zone was produced, by properly loading and exciting the transmitting antenna.[20] Thirdly, the signals in the region from 2000 to 3000 miles appeared more uncertain than in the region within the 2000 mile mark. The observations referred mainly to over-land waves and it would be of interest to repeat them with over-sea waves.

In general, for the shorter waves observations by many receiving stations in the United States indicate better signal reception in the region extending from the first skip zone to 2000 miles than in the region between 2000 and 4000 miles where at least one earth reflection is involved. At greater distances, however, from 5000 to 10,000 miles the short wave signals are very reliable, much more so than in the 2000 to 4000 mile zone. This is to be expected because, with increase of distance, there are a greater number of possible ray-paths connecting the transmitter and receiver, so that a local disturbance, such as a poor earth reflection, etc., of any one ray will have small influence on the signal. One might expect the inverse distance law of signal intensity to hold approximately in this region for the short waves.

[20] Van der Pol, Proc. Phys. Soc. London **29**, 269 (1916-1917).

At the antipodes of the earth there is a concentration of ray paths and a corresponding increase in signal strength. This has been frequently observed.

For radio communication over longer distances, of the interplanetary order, waves shorter than 40 meters would appear to be best able to pierce our own electron atmosphere as well as that of another planet. The circularly polarized long wave of Eq. (2) is of speculative utility, depending as it does on the intensity of magnetization of the electron atmosphere. Venturing even further into the realm of conjecture, the course of a ray proceeding in interplanetary space would be influenced by the electrons distributed from the sun. If this distribution were impartial in all directions, the electron density increases toward the sun, and the radio ray would be diverted towards the sun. It might pass beyond the influence of the sun after a small deflection, or it might spiral towards the sun until it reached that electron density requisite for total reflection, whereupon it would pursue an enlarging spiral until free again.

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THE STRUCTURE OF THE HYDROGEN MOLECULE ION*

By H. C. Urey

Abstract

The energies and dimensions of the hydrogen molecule ion for steady states in which the electron moves in orbits lying in the median plane between the two nuclei and perpendicular to the line joining them have been calculated. The steady states in which the electron moves in a straight line perpendicular to and through the mid point of the line joining the nuclei have energies which are given by the formula

$$W=-1.2300\ R_\infty h(1/n^{*2}),\quad n^*=1,\ 2,\ 3\ldots..$$

The normal state for which $n^*=1$, has the energy $W=-1.2300\ R_\infty h$, which agrees with the value calculated previously by Langmuir. Tables are given of the energy of each of the other steady states in which the electron moves in the median plane with angular momentum about the line joining the nuclei. These steady states are dynamically unstable on the basis of classical mechanics with respect to a displacement in the direction of the line joining the nuclei. It is found that Olson and Glockler's work on the ionizing potentials of hydrogen can be interpreted in such a way as to be consistent with these calculations. Five of their critical potentials agree with the calculated values for dissociation of the ion and resonance of the atom to the 3, 4, 5, 6, and 7th quantum states. The absence of the resonance to the second quantum state is consistent with the theory and the interpretation of their data. Two of their critical potentials agree with the theoretical values for resonance to the 3rd and 4th vibration quantum states of the ion and another to resonance to the 3rd circular orbit of the median plane. Their highest critical potential agrees with the calculated value for complete dissociation of the ion into two protons and an electron. The interpretation of the work of these men, which leads to the agreement with the theory, also gives a means of calculating a maximum value for the *heat of dissociation of the hydrogen molecule*, of 102, 500 cal. (4.43 volts), which agrees well with values secured by direct experimental methods. It is also shown that the dimensions of the model agree with values to be expected from a consideration of the moments of inertia of the hydrogen molecule in its excited states. The *calculated moment of inertia* of H^+_2 in its normal state is 2.60×10^{-41} g. cm^2.

1. Introduction

In his original papers on the structure of atoms and molecules, Bohr[1] considered a model for the hydrogen molecule ion consisting of two hydrogen nuclei and one electron moving in a circular orbit in the median plane between the two nuclei. The energy and dimensions of the model are fixed by the conditions that the angular momentum about the line joining the nuclei is an integral multiple of $h/2\pi$ and that the repulsive force of the nuclei on each other is equal to the component of the attractive force between the electron and one nucleus in the direction of the line joining the nuclei. He showed that this model would be dynamically unstable with respect to a blow in the direction of a line joining the nuclei or a small displacement from the median plane and therefore considered that this model was improbable. The energy and dimensions of the model as functions of the quantum number, derived by elementary methods, are given by Sommerfeld.[2]

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* A brief report of the work reported in this paper was presented before the National Academy of Sciences at Washington, D.C. on April 27, 1925, and appeared in the Proceedings of the National Academy of Sciences, Vol. 11, 618-621 (1925).

[1] N. Bohr, Phil. Mag. **26**, 857 (1913).

In 1922 Pauli[3] and Niessen[4] working independently again took up this problem and considered all the various types of orbits to be expected. The dynamically stable orbit was found to have the energy, $W = -0.5175\ Rh$, where R is the Rydberg constant. This corresponds to an ionizing potential of 7.00 volts for the ion and would lead to an ionizing potential of about 23 volts for the hydrogen molecule. Horton and Davies[5] by the method of electron bombardment subsequently found an inelastic collision at 22.8 volts, which they attributed to the ionization of the hydrogen molecule. Smyth[6] showed, however, by the positive ray method for ionizing potentials that no ions are produced in the neighborhood of this point. It seems therefore that the state calculated by Pauli and Niessen is not the normal state of the hydrogen molecule ion.

Pauli and Niessen did not calculate the energies of the states having the orbits in the median plane since, as they showed, these orbits are unstable with respect to the small displacement from this plane. Such a displacement would cause the electron to move in an orbit which would not lie in the immediate neighborhood of the original orbit. They emphasize the necessity of considering this condition of dynamic stability and their arguments would be entirely valid if atomic systems obeyed in all details the laws of classical mechanics. The work of several authors[7] on the helium atom is convincing evidence that this is not the case. If then we must discard the laws of classical mechanics for the complete description of the helium atom and atoms of higher atomic number and yet are able to use them for the description of the hydrogen and ionized helium atoms, it seems possible that some simple modification might make it possible to describe the hydrogen molecule ion. The stability of atoms and molecules in general, when considered from the standpoint of classical mechanics, is very surprising and rather suggests that this condition of dynamic stability should be the first to be modified. If these unstable orbits of the median plane of the hydrogen molecule ion exist, it probably means that there is no natural means of displacing the electron from its quantum orbits except by removing it to another quantum orbit, and that classical mechanics and the quantum conditions must be modified in such a way that these orbits are stable. The calculation of these orbits, as suggested here, can be regarded only as an incomplete description of this system.

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[2] A. Sommerfeld, Atomic Structure and Spectral Lines, 3rd ed. Appendix 14.

[3] W. Pauli, Jr., Ann. d. Physik **68,** 177 (1922).

[4] K. F. Niessen, Dissertation, Utrecht (1922); Ann. d. Physik **70,** 129 (1923).

[5] F. Horton and A. C. Davies, Phil. Mag. **46,** 872 (1923).

[6] H. D. Smyth, Proc. Roy. Soc. **105A,** 116 (1923).

[7] J. H. van Vleck, Phil. Mag. **44,** 842 (1922);
H. A. Kramers, Zeits. f. Physik **13,** 312 (1923);
M. Born and W. Heisenberg, Zeits. f. Physik **16,** 229 (1923);
A. Sommerfeld, Atombau und Spectrallienien, 4th ed. p. 197 (1924).

The application of quantum mechanics according to the original ideas of Bohr[1] and the quantum conditions of Wilson[8] and Sommerfeld[9] to the hydrogen and ionized helium atoms, both unperturbed by external fields and perturbed by homogeneous electric and magnetic fields, has been so successful, that it doubtless gives a close approximation to the truth. If then it is possible to describe the hydrogen molecule ion, using these same ideas and making only the modification with regard to the question of dynamic stability, it might serve as a stepping stone for the final solution of atomic mechanics.

Langmuir[10] suggested a model for the hydrogen molecule ion in which the electron is assumed to move in a straight line in the median plane perpendicular to and passing through the line joining the nuclei. He calculated the energy for the normal state of the ion and found it to be $-1.229\ Rh$. In the spring of 1925, the author without knowledge of Langmuir's previous work calculated the energy of this same model and found it to be $-1.2300\ Rh$ which is in excellent agreement with Langmuir's calculations and serves as an independent check for this quantity. Langmuir did not publish the detailed account of his calculation to my knowledge and therefore the details of my calculation will be given in this paper. The quantum conditions are applied according to the statement by Wilson[8] and Sommerfeld,[9] and the mean value of the component of the force of attraction between the electron and one nucleus in the direction of the line joining the nuclei is set equal to the force of repulsion between the two nuclei. The calculated values for the resonance and ionizing potentials agree with nine critical potentials observed by Olson and Glockler[11] within a few hundredths of a volt in all cases and suggest a consistent explanation of their results which is somewhat different from that given by the authors themselves. The interpretation of their work leads to a value for the heat of dissociation of hydrogen into its atoms which agrees well with determinations of this quantity by other methods.

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[8] W. Wilson, Phil. Mag. **29,** 795 (1915).

[9] A. Sommerfeld, Ann. d. Physik **51,** 1 (1916).

[10] I. Langmuir, Science **52,** 436 (1920).

The application of quantum mechanics to the hydrogen molecule ion with special reference to the orbits of the median plane is presented in paragraph 2. For further detail the reader should refer to the very complete work of either Pauli[3] or Niessen.[4] In paragraph 3 the experimental work on the ionizing potentials is reviewed and the agreement with the calculations is discussed. Paragraph 4 is a discussion of the possible structure of the hydrogen molecule and the relationship between the band spectrum of the hydrogen molecule and the structure of the hydrogen molecule ion.

2. The Application of Quantum Mechanics to the Hydrogen Molecule Ion with special Reference to the Orbits of the Median Plane

Charlier[12] has given a complete discussion of the dynamical problem of two fixed centers of force acting on a third with forces varying as the inverse square of the distance and Pauli and Niessen have discussed in detail the application of the quantum theory to this problem for the case of the hydrogen molecule ion. It is therefore unnecessary to repeat in detail their derivation of the formulas involved and only that necessary for the special class of orbits considered here will be repeated. The symbols used by these two authors differed. In this paper the symbols and general method used will be those of Pauli.

For the first approximation the nuclei may be regarded as having infinite mass and therefore as fixed. The energy and dimensions of the system will be determined by two sets of conditions, the quantum conditions applied to the motion of the electron and the condition that the mean force acting on the nuclei in the direction of the line joining them shall be equal to zero. The latter condition fixes the relative proportions of the model. The quantum conditions fix the absolute values.

[11] A. R. Olson and G. Glockler, Proc. Nat. Acad. Sci. **9**, 122 (1923).

[12] C. L. Charlier, Die Mechanik des Himmels, vol. 1, Chap. III, p. 122, Leipzig (1902).

The separation of variables for the problem of two fixed centers of force can be secured in elliptical co-ordinates. For the special class of orbits lying in the median plane the separation can be secured in plane polar co-ordinates in this plane with the origin at the point of intersection of the plane and the line joining the nuclei. Since these co-ordinates are somewhat more easily thought of, the dynamical equations can be set up in these co-ordinates. For purposes of integration it is convenient to change to the elliptical co-ordinates. The kinetic energy in polar co-ordinates is

$$T=\tfrac{1}{2}m(\dot{r}^2+r^2\dot{\phi}^2) \ ,$$

and the potential energy

$$V=e^2/2c-2e^2/\sqrt{r^2+c^2} \ ,$$

c being one half the distance between the nuclei. The Hamiltonian function is secured by substituting the momenta conjugate to r and φ for the $\dot{r}$ and $\dot{\varphi}$ in the kinetic energy and adding the potential energy.

$$H=\frac{p_r^{\ 2}}{2m}+\frac{p_\varphi^{\ 2}}{2mr^2}+\frac{e^2}{2c}-\frac{2e^2}{\sqrt{r^2+c^2}} \ . \tag{1}$$

The variables in this equation can be separated and the quantum conditions are

$$\oint p_r dr=J_1=n_1h \ , \qquad \oint p_\varphi d\varphi=J_3=n_3h \ , \tag{2}$$

where n_1 and n_3 are integral numbers and h is Planck's constant. The condition that the mean value of the force on the nuclei in the direction of the line of nuclei shall be zero is easily shown to be

$$\overline{\frac{e^2c}{(r^2+c^2)^{3/2}}}=\frac{e^2}{4c^2} \ , \tag{3}$$

the bar over the quantity indicating that the mean value is to be taken.

In order to perform the integrations it is convenient to change the variables from r and φ to λ and φ, λ being defined by the equation

$$\lambda=\sqrt{r^2+c^2}/c.$$

If λ were defined as the ratio of the sum of the two distances from the electron to the two nuclei to the distance between the two nuclei, it would define an ellipse. It is therefore one of the elliptical co-ordinates used by Pauli and Niessen. The change of co-ordinates can be made by a contact transformation derived from the function

$$V=p_r c\sqrt{\lambda^2-1}+p_\varphi \varphi\ .$$

The new conjugated variables are

$$r=\frac{\partial V}{\partial p_\varphi}=c\sqrt{\lambda^2-1}\ , \qquad p_\lambda=\frac{\partial V}{\partial \lambda}=p_r\frac{c\lambda}{\sqrt{\lambda^2-1}}=\frac{mc^2\lambda^2\dot{\lambda}}{\lambda^2-1}\ ,$$
$$\varphi=\frac{\partial V}{\partial p_\varphi}=\varphi\ , \qquad p_\varphi=\frac{\partial V}{\partial \varphi}=p_\varphi\ . \tag{4}$$

and the Hamiltonian function expressed in these co-ordinates is

$$H=\frac{\lambda^2-1}{2mc^2\lambda^2}p_\lambda{}^2+\frac{p_\varphi{}^2}{2mc^2(\lambda^2-1)}-\frac{2e^2}{c\lambda}+\frac{e^2}{2c}\ , \tag{5}$$

and this is equal to the total energy W, which is constant. The phase integrals (2) become

$$J_1=\sqrt{\alpha_1}\oint\frac{\sqrt{F(\lambda)}}{\lambda^2-1}d\lambda\ , \qquad J_3=\oint p_\varphi d\varphi=2\pi\alpha_3\ , \tag{6}$$

where the following substitutions have been made:

$$F(\lambda)=-\lambda^4+B\lambda^3+(1-A)\lambda^2-B\lambda\ , \tag{7}$$

$$\alpha_1=mce^2-2mc^2W\ , \qquad A=\frac{\alpha_3{}^2}{\alpha_1}\ , \qquad B=\frac{4e^2mc}{\alpha_1}\ . \tag{8}$$

The condition of Eq. (3) in the new co-ordinates is

$$\overline{\frac{1}{\lambda^3}}=\oint(1/\lambda^3)dt/\oint dt=1/4\ . \tag{9}$$

From Eq. (4) and the relation $p_\lambda=\sqrt{\alpha_1}\sqrt{F(\lambda)}/(\lambda^2-1)$, we find that

$$dt=\frac{mc^2}{\sqrt{\alpha_1}}\ \frac{\lambda^2 d\lambda}{\sqrt{F(\lambda)}}\ , \tag{9a}$$

and substituting this in (9), the condition for zero force acting on the nuclei in the direction of the line of nuclei becomes

$$\oint\frac{d\lambda}{\lambda\sqrt{F(\lambda)}}=\frac{1}{4}\oint\frac{\lambda^2 d\lambda}{\sqrt{F(\lambda)}}\ . \tag{10}$$

The integrals which have been indicated are elliptic integrals, which can be reduced to the standard forms by the usual change of variables.

If the roots of $F(\lambda)=0$ are $\lambda_1, \lambda_2, \lambda_3$ and λ_4, these can be arranged so that $\lambda_3<\lambda_4<\lambda_1<\lambda_2$, the limits of oscillation being λ_1 and λ_2. λ_3 can be expressed in terms of λ_1 and λ_2, thus

$$\lambda_3=-\frac{\lambda_1+\lambda_2}{1+\lambda_1\lambda_2}$$

and $\lambda_4=0$. The reduction to the normal form can be secured by changing to the variable z according to the equations

$$\lambda=\frac{\lambda_1}{1-nz^2}, \qquad n=1-\frac{\lambda_1}{\lambda_2}, \qquad k^2=\frac{\lambda_2-\lambda_1}{\lambda_2}\cdot\frac{-\lambda_3}{\lambda_1-\lambda_3}=n\frac{\lambda_3}{\lambda_3-\lambda_1}. \tag{11}$$

The integrals indicated in Eqs. (6) and (10), when expressed in terms of z, are

$$\int_{\lambda_1}^{\lambda_2}\frac{\sqrt{F(\lambda)}}{\lambda^2-1}d\lambda = 2\lambda_1^3n^2\sqrt{\frac{n}{(1-n)(n-k^2)}}\int_0^1\frac{(1-z^2)(1-k^2z^2)z^2}{(1-nz^2)(\lambda_1^2-(1-nz^2)^2)}\frac{dz}{\sqrt{(1-z^2)(1-k^2z^2)}}, \tag{12}$$

$$\int_{\lambda_1}^{\lambda_2}\frac{d\lambda}{\lambda\sqrt{F(\lambda)}}=\frac{2}{\lambda_1^2}\sqrt{\frac{(1-n)(n-k^2)}{n}}\int_0^1\frac{(1-nz^2)dz}{\sqrt{(1-z^2)(1-k^2z^2)}}, \tag{13}$$

$$\int_{\lambda_1}^{\lambda_2}\frac{\lambda^2d\lambda}{\sqrt{F(\lambda)}}=2\lambda_1\sqrt{\frac{(1-n)(n-k^2)}{n}}\int_0^1\frac{dz}{(1-nz^2)^2\sqrt{(1-z^2)(1-k^2z^2)}}. \tag{14}$$

The integrals[13] (13) and (14) can be expressed in terms of the elliptic

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[13] The following equations are used in securing Eq. (15):

$$\int_0^1\frac{(1-nz^2)dz}{\sqrt{(1-z^2)(1-k^2z^2)}}=\frac{n}{k^2}E-\frac{n-k^2}{k^2}K_1,$$

$$\int_0^1\frac{dz}{(1-nz^2)^2\sqrt{(1-z^2)(1-k^2z^2)}}=\frac{\lambda_1^2k^2}{2(1-n)(n-k^2)}\Pi(n\ ,\ k)+\frac{n}{2(1-n)(n-k^2)}E-\frac{1}{2(1-n)}K_1, \tag{15a}$$

$$\lambda_1=\frac{\sqrt{(2k^2-n)(n-2)+k^2}}{K}.$$

integrals of the first, second and third kinds and when so expressed and substituted in Eq. (10), this reduces to

$$\frac{\lambda_1^5}{8}\,\frac{k^2}{(1-n)\ (n-k^2)}\Pi(n,\,k)-\left(\frac{n}{k^2}\,E-\frac{n-k^2}{k^2}\,K\right)\left(1-\frac{k^2\lambda_1^3}{8(n-k^2)(1-n)}\right)=0, \tag{15}$$

where

$$K=\int_0^1\frac{dz}{\sqrt{(1-z^2)\ (1-k^2z^2)}},\qquad E=\int_0^1\sqrt{\frac{1-k^2z^2}{1-z^2}}dz$$

and

$$\Pi(n,\,k)=\int_0^1\frac{dz}{(1-nz^2)\ \sqrt{(1-z^2)(1-k^2z^2)}}\,.$$

The fraction

$$\frac{(1-z^2)(1-k^2z^2)z^2}{(1-nz^2)^2\ (\lambda_1^2-(1-nz^2)^2)}$$

in Eq. (12) can be broken up into simple fractions with the denominators $(1-nz^2)^2$, $1-nz^2$, $\lambda_1-(1-nz^2)$, and $\lambda_1+(1-nz^2)$. Then

$$\int_{\lambda_1}^{\lambda_2}\frac{\sqrt{F(\lambda)}}{\lambda^2-1}d\lambda=\lambda_1^3\sqrt{\frac{n}{(1-n)\ (n-k^2)}}$$
$$\left\{-\int_0^1\frac{2(n-k^2)(1-n)dz}{\lambda_1^2n(1-nz^2)\sqrt{(1-z^2)(1-k^2z^2)}}\right.$$
$$+\int_0^1\frac{2k^2dz}{n(1-nz^2)\sqrt{(1-z^2)(1-k^2z^2)}}+\left(\frac{3k^2}{n}-(1+k^2)-\frac{(n-k^2)\ (1-n)}{\lambda_1^2n}\right)$$
$$\frac{1}{\lambda_1}\left[\int_0^1\frac{dz}{(\lambda_1-1+nz^2)\sqrt{(1-z^2)(1-k^2z^2)}}\right.$$
$$\left.\left.+\int_0^1\frac{dz}{(\lambda_1+1-nz^2)\sqrt{(1-z^2)(1-k^2z^2)}}\right]\right\}$$

Using the Eq. (15a) and the above equation, we get

$$\int_{\lambda_1}^{\lambda_2}\frac{\sqrt{F(\lambda)}}{\lambda^2-1}d\lambda=\lambda_1^3\sqrt{\frac{n}{(1-n)(n-k^2)}}\left\{\frac{k^2}{n}\Pi(n,\,k)-\frac{1}{\lambda_1^2}E+\frac{n-k^2}{\lambda_1^2n}K\right.$$
$$+\left(\frac{3\,k^2}{n}-(1+k^2)-\frac{(n-k^2)(1-n)}{\lambda_1^2n}\right) \tag{16}$$
$$\left.\times\frac{1}{\lambda_1}\left[\frac{1}{\lambda_1-1}\,\Pi(n',\,k\ +\frac{1}{\lambda_1+1}\,\Pi(n'',\,k)\right]\right\},$$

where

$$n' = -\frac{n}{\lambda_1 - 1}, \text{ and } n'' = \frac{n}{\lambda_1 + 1}.^{14}$$

The limits of integration to be used. The systems which we are considering have a limiting degeneracy[15] since the electron moves in only one or two dimensions and therefore has only one or two frequencies in its motion. For the orbits in which the electron has angular momentum about the line of nuclei, the equation $F(\lambda) = 0$ has two roots which lie between $+1$ and $+\infty$. At these two points the momentum p_λ becomes zero; it is finite at all intermediate points and the variables λ and φ do not change rapidly with the time at any point between these two limits. The phase integral is to be extended from λ_1 to λ_2 and back to λ_1, or in polar co-ordinates from $r_{\min}$ to $r_{\max}$ and back to $r_{\min}$. These limits are similar to those used for the precessing elliptic orbits of hydrogen and are those used by Niessen in calculating orbits which do not lie in the median plane. The general character of such an orbit is shown in Fig. 1a illustrating the appearance of these orbits when viewed in the direction of the line of nuclei. The circles show the limits of oscillation, λ_1 being equivalent to $r_{\min}$ and λ_2 to $r_{\max}$.

As the angular momentum approaches zero, these orbits approach the vibration type of orbit. The root λ_1 of $F(\lambda) = 0$ becomes equal to 1, i.e. $r_{\min}$ becomes equal to zero and this does not represent a limit of libration. The system is similar in every way to the inharmonic oscillator. For this special type of orbit, it is necessary to use rectangular co-ordinates for determining the limits of integration. The p_λ is not equal to zero at $\lambda = 1$ or $r_{\min}$ equal to 0. It therefore does not represent a limit of oscillation and the phase integral must be extended from x_1 of Fig. 1b to x_2 and back to x_1, i.e. from $r_{\max}$ to $r_{\max}$ and back to $r_{\max}$. In terms of λ this is four times the integral from λ_1 to λ_2. The limits chosen are similar in every way to those commonly used for the inhar-

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[14] The formulas for expressing the complete elliptic integrals of the third kind occurring in this equation in terms of the complete and incomplete elliptic integrals of the first and second kinds are for $\Pi(n, k)$ and $\Pi(n'', k)$, in which $1 > (n \text{ or } n'') > k^2 > 0$,

$$\Pi(n,k) = \sqrt{\frac{n}{(1-n)(n-k^2)}}\left\{E(k', \beta)\, K(k) - F(k', \beta)[K(k) - E(k)]\right\},$$

where $\sin^2 \beta = \frac{n-k^2}{n(1-k^2)}$, and $k'^2 = 1 - k^2$, n'' being substituted for n throughout for $\Pi(n'', k)$, and for $\Pi(n', k)$, where $-\infty < n' < 0 < k^2 < 1$,

$$\Pi(n', k) = \sqrt{\frac{n'}{(1-n)(n'-k^2)}}\left\{\frac{\pi}{2} - E(k', \beta)\, K(k) + F(k', \beta)[K(k) - E(k)]\right\} + \frac{1}{1-n'}K(k),$$

where $\sin^2 \beta = 1/1 - n'$.

monic oscillator. It is easily seen that from the standpoint of the limits chosen for the orbits having angular momentum about the line of nuclei in the last paragraph, the orbits and steady states calculated using the limits of the phase integral chosen here are to be regarded as half quantum states.

Due to the difference in the limits over which the phase integrals are extended, as well as the greater simplicity of the equations for the vibration quantum states, it is convenient to discuss the vibration states and the states having angular momentum about the line of nuclei separately.

The vibration orbits. If the angular momentum about the line of nuclei is zero, $A=0$ and $F(\lambda)=-\lambda^4+B\lambda^3+\lambda^2-B\lambda$. The equation $F(\lambda)=0$ can be solved and has the roots

$$\lambda_1=1\ ,\qquad \lambda_2=B\ ,\qquad \lambda_3=-1\ ,\qquad \lambda_4=0\ .$$

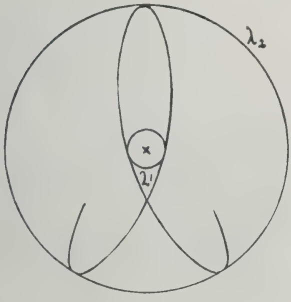

Fig. 1a

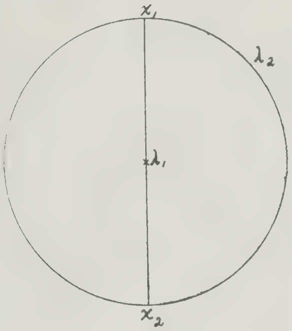

Fig. 1b

The change of variables by Eq. (11) then becomes

$$\lambda=1/(1-nz^2)\ ,\qquad n=1-1/B\ ,\qquad k^2=n/2\ ,$$

and Eq. (16) reduces to the simple form

$$\int_1^B\frac{\sqrt{F(\lambda)}}{\lambda^2-1}d\lambda=\tfrac{1}{2}\sqrt{2B}\,(\Pi(n\ ,\ k)-2E+K)\ .$$

Since this is 1/4 of the phase integral from x_1 to x_2 and back to x_1 the phase integral[16] J^* is

$$J^*=\sqrt{\alpha_1}\oint\frac{\sqrt{F(\lambda)}}{\lambda^2-1}d\lambda=2\sqrt{2B\alpha_1}\,(\Pi(n\ ,\ k)-2E+K)\ . \tag{17}$$

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[15] See M. Born, Vorlesungen über Atommechanik, Julius Springer (1925), Chap. 4, § 46.

[16] The asterisk will be used to designate the phase integrals and quantum numbers for which the limits of oscillation are x_1 and x_2 of Fig. 1b.

The condition for zero mean force acting on the nuclei in the line of nuclei from Eq. (15) becomes

$$\frac{B}{8}\Pi(n\ ,\ k)-(1-B/8)(2E-K)=0\ . \tag{18}$$

Since $a_1B=4\ mce,^2$ Eq. (17) gives for c/a

$$\frac{c}{a}=n^{*2}\frac{\pi^2}{8(\Pi(n\ ,\ k)-2E+K)^2}\ , \tag{19}$$

where a is the radius of the first quantum orbit of the hydrogen atom and $\Pi(n, k)$, E, and K satisfy Eq. (18). From Eqs. (19) and (8) the energy is found to be

$$W=-\frac{R_\infty h}{n^{*2}}\ \frac{8(\Pi(n\ ,\ k)-2E+K)^2}{\pi^2}\left(\frac{4}{B}-1\right)\ . \tag{20}$$

The Eqs. (19) and (20) give the distance between the nuclei and the energy as functions of B, which is the ratio of the maximum distance between the electron and one nucleus and half the distance between the nuclei. The solution of (19) or (20) and Eq. (27) simultaneously would give the distance between the nuclei or the energy, respectively, as a function of the quantum number and natural constants. The analytical solution of these simultaneous equations would be very difficult or impossible and it is therefore necessary to solve the equations by trial.

By trial a value of B has been found with satisfies Eq. (17). The values of K, E and $\Pi(n, K)$, which are functions of B, are then known and can be substituted in Eqs. (19) and (20). The results of the calculations are: $B=2.4297$, $K=1.71056$, $E=1.44795$, $\Pi(n, K)=2.7175$, and $c/a=0.5255\ n^{*2}$, $W=-R_\infty h\ 1.2300\ 1/n^{*2}$, and $\omega/\omega_0=(1/\omega_0)(\partial W/\partial J^*)=1.2300\ 1/n^{*3}$. In the last expression ω is the frequency of vibration of the electron in the hydrogen molecule ion and ω_0 is the frequency of revolution of the electron in the first quantum orbit of the hydrogen atom. The motion of the nuclei has been neglected, but the difference in energy due to the motion of the nuclei in the same direction as that in which the electron moves can be included in the formulae by using R_{H_2} instead of R_∞ in the formula given. This still neglects the effect of the motion of the nuclei in the direction of the line of nuclei. The calculation of B is believed to be accurate to about ± 0.0001. The value secured for the energy ($W=-1.2300\ R_\infty h$) agrees well with Langmuir's result ($W=-1.229\ Rh$) as noted above.

The orbits of the median plane having angular momentum about the line of nuclei. For these orbits the phase integral is extended from

λ_1 to λ_2 and back to λ_1 and therefore the integral given in Eq. (16) must be multiplied by 2 in order to extend this integral over a complete cycle of the motion. For this case

$$F(\lambda)=-\lambda^4+B\lambda^3+(1-A)\lambda^2+B\lambda\ .$$

If we divide the Eq. (6)

$$J_1=\sqrt{\alpha_1}\oint\frac{\sqrt{F(\lambda)}}{\lambda^2-1}d\lambda$$

by

$$J_3=2\pi\sqrt{A\,\alpha_1}$$

from Eqs. (6) and (8), we get

$$J_1/J_3=\frac{1}{2\pi\sqrt{A}}\oint\frac{\sqrt{F(\lambda)}}{\lambda^2-1}d\lambda\ , \tag{21}$$

the latter integral being expressed in terms of the complete elliptic integrals by (16). The condition that the force acting on the nuclei in the direction of the line of nuclei shall be zero is given by Eq. (15). These two simultaneous equations have been solved by trial, a value of λ_1 first being chosen and then by trial a value for λ_2 found which would satisfy Eq. (15). In this way a number of pairs of such values of λ_1 and λ_2 were found and the ratio J_1/J_3 was calculated from Eq. (21) for these pairs of values of λ_1 and λ_2. From the equation

$$-\lambda^4+B\lambda^3+(1-A)\lambda^2-B\lambda=(\lambda-\lambda_1)(\lambda-\lambda_2)(\lambda-\lambda_3)(\lambda-\lambda_4)$$

expressions for A and B in terms of λ_1 and λ_2 can be derived and these are

$$A=\frac{(\lambda_1^2-1)(\lambda_2^2-1)}{1+\lambda_1\lambda_2}\ ,\qquad B=\frac{(\lambda_1+\lambda_2)\lambda_1\lambda_2}{1+\lambda_1\lambda_2}\ .$$

By eliminating α_1 from the expressions for A and B of Eq. (8), c can be secured as a function of A and B, and by eliminating α_1 and c from the three expressions of Eq. (8) and substituting for α_3 from Eq. (6) the energy can be given as a function of A and B, and these are respectively

$$c/a=\frac{B}{4A}n_3^2$$

$$W=-\frac{1}{n_3^2}\,\frac{4A}{B}\left(\frac{4}{B}-1\right)Rh$$

The quantities $4A/B\ (4/B-1)$ and $4A/B$ were plotted against the ratio n_1/n_3 for the region in which n_1/n_3 is small and against n_3/n_1 in the region in which this is a small quantity. Smooth curves were drawn through the points and the values of $4A/B\ (4/B-1)$ and $4A/B$ for the values of n_1/n_3, which are the ratios of integral numbers, were read from the curves. The values of $4A/B\ (4/B-1)$ and $B/4A$ so secured are given in Table Ia.

TABLE Ia

n_1/n_3	$\frac{4A}{B}(\frac{4}{B}-1)$	$B/4A$	n_3
1	0.130	5.10	1
2	0.048	13.5	1
3	0.025	26.	1
4	0.015	42.	1
5	0.011	60.	1
1/2	0.280	2.44	2
3/2	0.074	8.85	2
5/2	0.034	19.2	2
1/3	0.382	1.82	3
2/3	0.209	3.22	3
4/3	0.088	7.50	3
5/3	0.064	10.3	3
1/4	0.445	1.58	4
3/4	0.183	3.65	4
5/4	0.096	6.85	4
1/5	0.489	1.45	5
2/5	0.337	2.04	5
3/5	0.235	2.90	5
4/5	0.170	3.92	5

In Table Ib are listed the values of $-W/Rh$ for the orbits of the median plane for values of n_1 and n_3 from 1 to 5. The numbers given in the first column are those of the even values of n^* only since only these numbers are comparable to the other quantities in the table due to the difference in the limits over which the phase integral is extended.

TABLE Ib

$n_1 \downarrow$ $n_3 \rightarrow$	0	1	2	3	4	5
0		.8777	.2194	.0975	.0549	.0351
1	.3075($n^*=2$)	.130	.070	.0424	.028	.020
2	.0769($n^*=4$)	.048	.032	.0232	.0175	.0135
3	.0342($n^*=6$)	.025	.0185	.0144	.0114	.0094
4	.0192($n^*=8$)	.015	.0120	.0098	.0081	.0068
5	.0123($n^*=10$)	.011	.0085	.0071	.0060	.0052

3. COMPARISON WITH EXPERIMENT

The data on the ionizing and resonance potentials of molecular hydrogen are very discordant both with regard to the numerical values reported and the interpretation of these values. The ionizing potentials reported in the literature vary from approximately 11 volts to 16.68 volts, with rather consistent agreement between a number of observers for the potentials[17] 11, 13.5 and 16.0 volts. It is very difficult to explain the ionization at 11 volts. That at 13.5 is usually attributed to atomic hydrogen which has diffused from the region of the hot filament to the point where the inelastic collisions take place. The third potential at 16 volts is usually assumed to be the ionizing potential of the molecule or the dissociation of the molecule and ionization of one of the atoms. The latter assumption gives about 2.5 volts for the dissociation potential of the molecule and this does not agree with the values secured by other methods. The agreement between the different authors is rather rough and the results of Olson and Glockler[11] are at variance apparently with the work of all other authors. The wide differences secured by different observers indicates that the method of inelastic collisions possibly gives only approximate values for the energy changes in resonance, dissociation, and ionization of molecules.

Olson and Glockler have measured, apparently with great accuracy, nine critical potentials of hydrogen between 14.84 and 16.68 volts, the latter potential having been duplicated in eight runs with a maximum variation of .11 volt. Six of these potentials can be represented by the formula

$$v=3.16+13.52(1-1/n^2), \qquad n=3,\ 4,\ 5,\ 6,\ 7 \text{ and } \infty \quad \cdot\ \cdot\ \cdot\ \cdot$$

As 13.52 is the ionizing potential of the hydrogen atom these authors assumed that these critical potentials were due to dissociation plus resonance of one atom, the dissociation potential being 3.16 volts. Resonance to the second quantum state of the atom was not observed and no explanation of this was given nor has any satisfactory explanation of this unexpected result been found since their paper was published. The remaining three potentials were assumed to be resonance potentials of the molecule. Two of these potentials can be represented by the formula

$$v=16.68(1-1/n^2), \qquad n=3, \text{ and } 4, \quad \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot$$

and if $n=\infty$ is substituted in this formula it gives the same potential as that for $n=\infty$ in the preceding equation. The constant in this equation is the highest potential observed. This relationship was pointed out to me by Dr. A. R. Olson in 1923 at the time their paper was published. It is immediately evident that if these two empirical relations are true, then not only the differences in the potentials observed by Olson and Glockler, but also the absolute magnitude of these potentials must be correct, for if a constant is added to the first equation, then the potential secured by setting $n=\infty$ in this equation will no longer give the constant to be used in the second equation. The latter must then be written in the form

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[17] See Bull. Nat. Res. Council, vol. 9, Part 1, No. 48, Critical Potentials by K. T. Compton and F. L. Mohler.

$$V=16.68\ (1-1/n^2)+\text{constant}$$

and the simplicity of Olson and Glockler's equations is lost.

No difference can be seen in the one curve published by Olson and Glockler between breaks in the curve corresponding to resonance of the molecule and those corresponding to dissociation and resonance of the atom. If these critical potentials represented by the former equation were also due to resonance without dissociation, this would be in exact accord with the work of Glitscher[18] on the many lined spectrum of hydrogen. His work indicates that there are steady states of some emitter of the many lined spectrum which differ from each other by the same amounts as the steady states of the hydrogen atom.

The very close agreement between the results of these observers and the potentials predicted from the theory of the hydrogen molecule ion is quite remarkable and if it is possible to interpret their critical potentials as being due to the hydrogen molecule ion instead of the hydrogen molecule, it indicates that a very high precision has been secured by these authors. For dissociation of the ion and resonance of the atom the potentials predicted from theory can be represented by the formula

$$v=3.12+13.53(1-1/n^2),\ n=2,\ 3,\ \cdots\cdots\cdots$$

and the theoretical formula for the resonance potentials of the hydrogen molecule ion (vibration quantum states only) is

$$v=16.65(1-1/n^{*2}),\ n^*=2,\ 3,\ \cdots\cdots\cdots\cdots$$

It is necessary, however, to interpret the experimental results in quite a different way from that given by the authors themselves. The calculated and observed potentials together with the interpretation given by Olson and Glockler and that given here are shown in Table II. The numbers in parenthesis refer to the quantum numbers of the steady states. The first number given in parenthesis after the hydrogen molecule ion is n_1, the quantum number conjugate to the λ co-ordinate, the second is n_2, the number conjugate to the μ co-ordinate of Pauli which is always zero for the orbits of the median plane, and the third is the n_3, the quantum number conjugate to the φ co-ordinate. The critical potential at 15.35 volts has been shown as resonance to the third circular orbit level. It seems to fit this transition better than any other calculated, but since only this one resonance out of all the possible rotation orbit levels appears in the experimental data, some other explanation may be possible. It may be also that the critical potentials given as dissociation and resonance of the atom are really resonance potentials as suggested above. No energy levels of the hydrogen molecule ion which have been calculated either by Niessen or by me give this simple relation, i.e. differences in energy levels equal to the differences in energy levels of the hydrogen atom. Since the mechanics which has been used is admitted to be incomplete, the possibility that these are resonance potentials of the ion is not excluded. Such a relationship is more likely to be characteristic of the hydrogen molecule ion than of either the hydrogen molecule or the triatomic hydrogen molecule or its ion, because the relatively simple structure of the hydrogen molecule ion would lead us to expect simpler relationships between the steady states.

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[18] K. Glitscher, Sitzungsber. der Bayer. Akad. 1916, p. 125, See A. Sommerfeld, Atombau und Spectrallinien, 4th ed. pp. 92, 93, Friedr. Vieweg and Sohn (1924).

TABLE II

Resonance potentials of the hydrogen molecule ion

Reaction (Olson and Glockler)	Reaction (Urey)	Potentials	
		obs.	calc.
$H_2=H(1)+H^++e$	$H_2^+(1^*,0,0)=H^++H^++e$	16.68	16.65
$H_2=H(1)+H(7)$	$H_2^+(1^*,0,0)=H^++H(7)$	16.41	16.37
$H_2=H(1)+H(6)$	$H_2^+(1^*,0,0)=H^++H(6)$	16.33	16.28
$H_2=H(1)+H(5)$	$H_2^+(1^*,0,0)=H^++H(5)$	16.11	16.11
$H_2=H(1)+H(4)$	$H_2^+(1^*,0,0)=H^++H(4)$	15.84	15.80
$H_2=H_2(r)$	$H_2^+(1^*,0,0)=H_2^+(4^*,0,0)$	15.62	15.61
$H_2=H_2(r)$	?$H_2^+(1^*,0,0)=H_2^+(0,0,3)$	15.35	15.33
$H_2=H(1)+H(3)$	$H_2^+(1^*,0,0)=H^++H(3)$	15.12	15.15
$H_2=H_2(r)$	$H_2^+(1^*,0,0)=H_2^+(3^*,0,0)$	14.84	14.80
....	$H_2^+(1^*,0,0)=H^++H(2)$	.....	13.27
....	$H_2^+(1^*,0,0)=H_2^+(2^*,0,0)$	.....	12.49

The apparatus of Olson and Glockler is adapted for the detection of resonance potentials and not ionization potentials. Their lowest potential is 14.84 volts and it seems very probable that this is greater than the first resonance potential of the hydrogen molecule. Other observers have reported critical potentials as low as 10 volts. For some reason these do not appear in Olson and Glockler's work nor do they observe the potential corresponding to dissociation and resonance of the atom to the second quantum orbit for which the calculated value is 13.27 volts (See table II). In a previous note it was assumed that the current measured by their electrometer was due to ions, no current would be observed until the H_2^+ ion was produced by an electron of velocity between 13.27 and 14.84 volts. Due to an error in their paper this interpretation is no longer tenable.[19] It is still possible that only light emitted by the H_2^+ ion reaches the electrometer electrode, the light produced by resonance of the molecule being absorbed by the layer of hydrogen gas between the point of excitation and the detecting electrode. Though this interpretation is open to objections, the experimental fact remains that the lowest potential observed by these authors is 14.84 volts and this is probably much larger than the first resonance potential of the molecule. This point together with others appearing in their work must be decided by further experiment. For the present we assume that all potentials observed by these men are due to the hydrogen molecule ion.

This interpretation of this experimental work gives an explanation of one of its peculiarities, namely the absence of the critical potential for dissociation and resonance of the atom to the second quantum state for which the calculated value is 13.27 volts. For if the ionizing potential of the molecule is greater than this potential, no current would be observed until this point was exceeded and thus it would not be observed. This interpretation is possible quite independently of any theoretical considerations, but leads to the conclusion that the ionizing potential of the molecule lies between 13.27 and 14.84 volts, and this appears to be in disagreement with the work of other observers.

TABLE III

Run	Initial correction	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*	*i*
1	2.29		15.30			15.86	16.02		16.40	16.70
2	3.18	14.75	15.09	15.34		15.79	16.19			16.68
3	.75	14.89	15.09	15.44	15.74		16.14	16.34		16.71
4	1.39		15.25		15.61	15.92	16.16	16.33		16.68
5	1.24	14.75	14.97	15.29	15.56	15.85	16.05		16.32	16.63
6	1.28		15.17	15.41	15.70	15.89	16.14	16.36	16.56	16.73
7	1.61	14.94		15.33	15.54	15.78	16.10	16.35		16.70
8	2.08	14.89	15.08	15.28	15.56	15.76			16.38	16.62
Av.		14.84	15.12	15.35	15.62	15.84	16.11	16.33	16.41	16.68
Theor.		14.80	15.15	15.33	15.61	15.80	16.11	16.28	16.37	16.65

The complete experimental data of Olson and Glockler are given in Table III. The first column gives the run number, the second the initial correction applied, and the remaining columns the observed potential plus the initial correction of column 2. The arrangement into groups *a*, *b*, *c*, etc. is the same as that given by the authors in their Table II.

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[19] In a conversation between Dr. Olson and the author an error was discovered in the paper of Olson and Glockler. In their Fig. 1 the accelerating and retarding potentials A_4 and R_4, which are shown between gauzes G_3 and G_4, should be placed between P and G_4 and the zero field $A_5=0$ should have been placed between G_3 and G_4. The space between G_3 and G_4 is in effect a Faraday cage. This makes the interpretation of these potentials given by the author in the Proceedings of the National Academy of Sciences, Vol. 11, 618 (1925) an impossible one.

The first critical potential observed varied from 14.75 to 15.30 volts. Had they regarded these as being the same critical potential, they would have concluded that the ionizing potential was about 15 volts with an experimental accuracy of ±.3 volt. This would be the usual interpretation and the limits of error would have been much the same as that secured by other observers. The highest potential observed is shown in the last column. When this is regarded as the constant critical potential, it is possible to arrange the ones preceding in groups which show fair agreement among themselves. The averages of these potentials are listed in Table III. The listing of the two columns *g* and *h* separately is rather artificial, since the points on the curves were read only at .1 volt intervals, and several other changes in arranging the observed potentials might be made as for example the first potential of column *b*, but on the whole it seems difficult to rearrange the data in any better way than that given by the authors.

There is then an erratic variation of the lowest potential observed for which there seems to be no satisfactory explanation. Richardson and Tanaka[20] have pointed out a similar difficulty in their work on the ionizing potentials of hydrogen. They say, "An examination of the data leads to the conclusion that the observed oscillation of the values between 14.6 and 15.4 volts is real and not due to errors in drawing the curves. In other words, the measured potentials may have been changing by an extreme amount of 0.8 volt in the course of these experiments." This statement can be applied without change to the first potentials recorded in Table III. Due to this variation, we are not justified in taking 14.84 volts as the ionizing potential of the molecule, but only in regarding this as a maximum. Using this interpretation, it is possible to calculate a maximum value for the energy dissociation of hydrogen gas by the following equations:

$$
\begin{array}{lll}
 & H_2 = H_2^+ + e & ;\ 14.84 \text{ volts (experimental)} \\
 & H_2^+ = 2H^+ + e & ;\ 16.65 \text{ volts (theoretical)} \\
\cline{2-3}
\text{adding} & H_2 = 2H^+ + 2e & ;\ 31.49 \text{ volts} \\
\text{and subtracting} & 2H = 2H^+ + 2e & ;\ 27.06 \text{ volts } (= 2\,Rh) \\
\cline{2-3}
 & H_2 = 2H & ;\ \ 4.43 \text{ volts } (= 102{,}500 \text{ cal.})
\end{array}
$$

A comparison of this value with that secured by other methods is given in Table IV.

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[20] O. W. Richardson and T. Tanaka, Proc. Roy. Soc. **106A**, 640 (1924).

The value calculated here is somewhat larger than the other values given in the table. If 93,000 cal. (=4.03 volts) is about the correct value for the heat of dissociation the ionizing potential of the hydrogen molecule should be about 14.3 volts. If the 13.5 volts ionizing potential observed by several authors is made to coincide with this value by adding .8 volt, then the 16 volt potential will agree with the ionizing potential calculated for the hydrogen molecule ion. This is a possible explanation of the ionizing potential data.

TABLE IV

Author	Method	Heat of dissociation
Langmuir[21] (1915)	Conduction from a hot wire	84,000 cal.
Isnardi[22] (1915)	Conduction from a hot wire	100,000 cal.
Wohl[23] (1924)	Temperature of explosions	90,000 cal.
Olson and Glockler and from this paper	Ionizing potentials	102,500 cal. (Maximum)

The interpretation of these critical potentials suggested here, requires that the first process occurring is

$$H_2 = H_2^+ + e$$

and that the H^+ ions are produced by a second collision. This is in agreement with the work of Smyth[24] on the ionizing potentials of hydrogen by the method of positive ray analysis and that of Hogness and Lunn[25] using the same method. These authors conclude that the first ions produced are H_2^+ and that the H^+ ion is produced by collisions with other molecules. Smyth thinks however that the hydrogen molecule ion is energetically unstable with respect to the atom and atomic ion. This would be in disagreement with the theory. Hogness and Lunn think that their experiments are inconclusive on this point. The potentials at which the H_2^+ ion appears are somewhat higher than 14.84 volts though both authors question their absolute values.

No spectroscopic confirmation of the theory has been found up to the present. The theory predicts an ultraviolet limit of 741A. Hopfield[26] found an ultraviolet limit of 885A, which is equivalent to 13.94 volts or 1.030 *Rh*. This would be about the limit to be expected for the molecular spectrum if its ionizing potential is about 14.3-14.5 volts.

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[21] Irving Langmuir, J. Am. Chem. Soc. **37**, 417 (1915).

[22] T. Isnardi, Zeits. f. Elektrochemie, **21**, 405 (1915). Wohl corrected a slight error in computation in Isnardi's work. See following reference.

[23] K. Wohl, Zeits. f. Elektrochemie **30**, 49 (1924).

[24] H. D. Smyth, Phys. Rev. **25**, 452 (1925).

[25] T. R. Hogness and E. G. Lunn, Proc. Nat. Acad. Sci. **10**, 398 (1924) and Phys. Rev. **26**, 44 (1925).

[26] J. J. Hopfield, Phys. Rev. **20**, 573 (1922).

The absence of the ultraviolet spectrum of H_2^+ may be due to an extremely low intensity, though if Olson and Glockler can observe the ionizing potentials of the H_2^+ ion, it should be possible to secure the spectrum.

The theoretical work is being continued to see whether it is possible to calculate part of the many lined spectrum of hydrogen by including the contribution of the rotation and vibration of the nuclei to the energy and the change of energy of the electron due to the motion of the nuclei. For the special case of the rotation of the nuclei about the line of vibration of the electron in the vibration orbits, it seems possible to do this without modifying classical mechanics. For the other orbits of the median plane, it seems that some modification of the laws of mechanics must be made.

I also expect to attempt a repetition of the experimental work of Olson and Glockler and possibly some extensions to the resonance states of the ion which should appear theoretically below the ionizing potential of the molecule.

4. The Structure of the Hydrogen Molecule

Since the attempts to calculate the ionizing potential of the helium atom have been unsuccessful, it is very doubtful whether any similar calculations on the hydrogen molecule would be any more successful. But whatever the structure of the normal hydrogen molecule may be, the adiabatic removal of one electron must leave the hydrogen molecule ion in its normal state. If then this normal state of the hydrogen molecule ion is the one suggested here, we can describe the hydrogen molecule as consisting of two nuclei and two electrons, vibrating in approximately straight lines in the median plane between the two nuclei. The two electron orbits may be oriented toward each other at some angle possibly a right angle and may be moving with phases such that the one is at the line joining the nuclei while the other is farthest from this line. Such a model would be diamagnetic. We can speak of such a model only with about the same certainty as we can of the crossed and coplanar models of helium.

The moment of inertia of the hydrogen molecule in its normal state should always be larger than the moment of inertia of the hydrogen molecule in any of its stationary states. When the second electron of the hydrogen molecule is in one of the higher quantum states, the component of its force of attraction on the nuclei in the direction of the line of nuclei would be small and therefore the difference in the moments of inertia of the hydrogen molecule ion and of the hydrogen molecule in its excited states should be small. In Table IV are given the moments of inertia and distances between the nuclei of the Bohr, Pauli and Niessen and the vibration models of the hydrogen molecule ion and of the excited hydrogen molecule calculated from the Fulcher bands by Allen.[27] These quantities calculated for the vibration model of the ion agree well with those to be expected by comparison with those calculated by Allen for the hydrogen molecule.

TABLE IV

		Moment of inertia (g. cm.$^2\times 10^{41}$)	Distance between nuclei (cm.$\times 10^8$)
H_2^+(0,0,1)	(Bohr)	7.05	.921
H_2^+(0,1,1)	(Pauli and Niessen)	72.0	2.942
H_2^+(1,*0,0)	(Langmuir and Urey)	2.600	.559
H_2 (First Fulcher Bands)		$I_i=1.794$	$d_i=$ .462
		$I_f=1.862$	$d_f=$ .470
H_2 (Second Fulcher Bands)		$I_i=1.249$	$d_i=$ .385
		$I_f=1.292$	$d_f=$ .392

Dieke[28] and Takahashi[29] have given very different interpretations to the Fulcher bands than those used by Allen and originally suggested by Lenz.[30] Dieke shows that the so-called Fulcher triplets can be extended and arranges these triplets and other lines as one branch of a band to which he has added another branch. The differences in frequencies which have been usually regarded as due to differences in the rotational energy changes are on Dieke's view to be correlated with vibrational changes in energy. This would make the moments of inertia calculated by Allen entirely meaningless. However, other methods[31] of calculating the moments of inertia as from the heat capacity and entropy give values of the same order of magnitude as those secured by Allen.

This model of the hydrogen molecule also suggests that the non-polar bond of chemists may be regarded as two electrons vibrating in a plane between the two atoms perpendicular to the line joining their nuclei. Such a picture would be a very satisfactory one from the standpoint of chemists, though of course no more so than a similar extension of the Bohr-Debye model of the hydrogen molecule.

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[27] H. S. Allen, Proc. Roy. Soc. **106A,** 69 (1924).

[28] G. H. Dieke, Amsterdam Acad. **27,** 490 (1924); Phil. Mag. **50,** 173 (1925); Zeits. f. Physik. **32,** 180 (1925).

[29] Takahashi, Jap. Journ. of Phys. **2,** 95 (1923).

[30] W. Lenz, Verh. d. D. Phys. Ges. **21,** 632 (1919).

[31] See F. Reiche, Ann. d. Physik. **58,** 657 (1919).
E. C. Kemble and J. H. VanVleck, Phys. Rev. **21,** 653 (1923).
H. C. Urey, J. Amer. Chem. Soc. **45,** 1445 (1923).

There are four points of agreement between calculation and experiment which can be regarded as independent: first, the ionization potential calculated agrees with the experimental value and it immediately follows that the calculated values for dissociation and resonance of the atom must agree with these experimental critical potentials; second, the resonance potentials of the hydrogen molecule ion as calculated agree with the experimental critical potentials; third, the heat of dissociation of the hydrogen molecule calculated agrees with the experimental values; and fourth, the moment of inertia of the hydrogen molecule ion agrees with the values expected from the moment of inertia of the excited hydrogen molecule.

My thanks are due to Dr. G. Breit of the Carnegie Institution of Washington for his friendly criticism of this work and for repeating much of the mathematical work and to Dr. E. C. Kemble and Dr. J. C. Slater of Harvard University for their criticism of this paper, and valuable suggestions made in regard to it.

Johns Hopkins University,
Baltimore, Md.
October 20, 1925.

BOOK REVIEWS

A Treatise on Light. (Fourth edition). R. A. HOUSTOUN.—The popularity of this standard text is shown by the fact that it has passed through three editions in the last four years. The total changes, however, have been relatively slight and the present edition differs from the last only in the fact that five or six pages in the section on Spectroscopy have been rewritten and a few minor improvements introduced elsewhere. The many friends of the book will welcome, when the time comes a more thorough revision, with the incorporation in the body of the text of material on recent advances such as is now added in a special chapter at the end of the volume.—Pp. xi+486, 334 figs., Longmans, Green & Co., New York, 1925. Price $4.20.

L. R. INGERSOLL

Physikalische und technische Grundlagen der Roentgentherapie. G. GROSSMANN —This book is intended primarily for the radiologist but deals only with the physical and technical aspects of the subject. It contains a comprehensive survey of the field in its present stage of development, particularly as regards German contributions.

The first part of the book is devoted to a general discussion of x-radiation and methods of measurement. Numerous quantitative data are given. The presentation of the dosage problem leaves much to be desired.

The second part is devoted to a discussion of x-ray tubes, high voltage machines and measuring instruments. With two or three exceptions all the apparatus described is of German manufacture. The principles involved, which apply also to American apparatus, are treated extensively.

The subject matter is presented in simple language, using mathematics sparingly and illustrations copiously. The book, therefore, should prove of considerable value to the radiologist. The physicist who wishes to familiarize himself with the problems of x-ray therapy will find it of great assistance.—Pp. viii+300, 207 illustrations, Urban & Schwarzenberg, Berlin, 1925. Price $13.50.

C. G. FAILLA

Über die Synthese der Feldspatvertreter. W. EITEL. Preischriften von der Fürstlich Jablonowskischen Gesellschaft, LII.—The feldspathoids, according to the definition of the author, are a group of minerals closely related to the feldspars in composition and petrogenesis, and thus defined include not only the alkali aluminosilicates such as leucite and nephelite, but also the melilites and the minerals of the sodalite group. The components thus include the common rock-forming oxides Na_2O, K_2O, CaO, MgO, Al_2O_3 and SiO_2, as well as the less common components CO_2, SO_3, S, and NaCl, and it is evident that a comprehensive treatment of the feldspathoids necessitates a discussion of the greater portion of our knowledge of mineral chemistry. Such a discussion has been given, and the author's first-hand experience both in petrology and in physical chemistry has enabled him to give a well-balanced analysis of the material in the literature, which consists of two portions of widely differing character. The first portion comprises the work of the older school, whose mineral syntheses were oftentimes carried out by most ingenious methods, but by methods which bore no possible relation to the natural mineral paragenesis. The second portion includes the precise physicochemical researches of the past two decades, which have yielded much information concerning various binary and ternary systems containing the above common rock-forming oxides. The discussion of this material is particularly full. The third portion of the book consists largely, of work in which the author has been active, the introduction of volatile components, particularly CO_2, into mineral systems; work which has served to show the physico-chemical relationship of the complex mineral cancrinite and the more usual compounds calcite, sodium carbonate and nephelite. This book is to be recommended to all interested in the problems of mineral chemistry and their study from the standpoint of physical chemistry. The indexing has been well done.—Pp. viii+258, Akademische Verlagsgesellschaft m.b.H, Leipzig, 1925. GEORGE W. MOREY

Photoelectricity. (Second Edition). H. S. ALLEN.—The first edition of Allen's "Photoelectricity," published in 1913, has been almost the only work in English dealing in a comprehensive manner with all aspects of the subject. Since 1913 the subjects of atomic structure and radiation have experienced an extraordinary development which might well be expected to make any text quite out of date, which dealt with phenomena occurring as the result of the irradiation of matter. The author of this book, while recognizing this situation in principle yet finds the facts of photoelectricity and the deductions to be drawn from them substantially unaltered. Another way of stating this might be that the true nature of photoelectric action is no more understood now than then. Proceeding on this basis the size, arrangement and illustrations of the new edition closely follow the old. The first nine chapters describe the early experiments, methods of measurement, the typical phenomena in various types of cells and with various kinds of illumination. These chapters are followed by an interesting series of reviews of allied subjects such as fluorescence and phosphorescence, photography and physiological effects, in which photoelectric action may be considered to play an important part.

A criticism to which the book, being professedly a second edition, is open, is that by its retention of the original illustrations, with exceedingly few additions, the perspective of the presentation suffers. Recent work is not only relatively poorly illustrated, but its description, for lack of appropriate diagrams, is much less thorough and intelligible than is the case with early work. Deletion of portions of the chapter on photoelectric fatigue, now a subject largely of historical interest, elimination of detailed discussion of phenomena which have turned out to be due to poor experimental technique, and more critical discussion of later work in place of the very rapid general review with which much of this is presented, would make the book more valuable to serious students.

The references given are commendably complete, and practically all important work on the subject is given some mention. A full bibliography of papers since 1913, and appendices containing useful constants and relationships enhance the value of the book. It should prove a very valuable book for those who wish an introduction to the subject. —Pp. xi+320, 43 figs. Longmans, Green & Company, New York, 1925. Price $6.50.
HERBERT E. IVES

A Condensed Collection of Thermodynamic Formulas. P. W. BRIDGMAN.—This collection covers the 10 most frequently used variables, with the equations formed from them and their first and second derivatives. The possible number of such equations is very great, too great to be listed in detail. Bridgman has succeeded by a relatively simple classification in reducing the number of equations to be listed so that they are readily printed and correspondingly readily used. To use the tables, this classification must be mastered—a task well worth while, for its comprehensive survey of the group of relations, and the added mastery over them. Solutions for a number of problems are given to illustrate the use of the tables. Workers in this field should find the book of material help both in finding desired relations and in permitting a comprehensive survey of the group of relationships related to the problem in hand.—Pp. 34, Harvard University Press, Cambridge. Price $1.50. J. R. ROEBUCK

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE KANSAS CITY MEETING,

DECEMBER 28, 29, AND 30, 1925

The twenty-seventh annual meeting (136th regular meeting) of the American Physical Society was held at Junior College, Kansas City, Missouri, on Monday, Tuesday and Wednesday, December 28, 29, and 30. The presiding officers were Professor Dayton C. Miller, President of the Society, and Professor K. T. Compton, Vice-President. The attendance was about one hundred and fifty.

On Tuesday afternoon at four o'clock, Professor Dayton C. Miller delivered the presidential address on "The Michelson-Morley Ether-drift Experiment—Its History and Significance," in the Assembly Room of the Junior College. This address was a general session of the A.A.A.S.

The annual joint session with Section B was held on Wednesday morning, with Professor H. M. Randall, Chairman of Section B, presiding. The retiring Vice-President, Professor K. T. Compton, opened the joint meeting with an address entitled "Dielectric Constants and Molecular Structure." This was followed by a symposium on "Relativity," consisting of three addresses as follows: "The Effect of the Earth's Rotation on the Velocity of Light," by H. G. Gale, University of Chicago; "Astronomical Evidence for Gravitational Displacement of Spectrum Lines," by Charles E. St. John, Mt. Wilson Observatory; "Experimental Science and World Geometry," by A. C. Lunn, University of Chicago. In the absence of Professor Gale, owing to illness, his paper was read by Dr. W. W. Watson.

On Tuesday evening, December 29, 1925, there was a dinner for the members of the Society and of Section B and their friends at the Hotel Baltimore, attended by ninety-eight persons.

Annual Business Meeting.—The regular annual business meeting of the American Physical Society was held on Tuesday morning, December

29, 1925, at eleven o'clock. A canvass of the ballots for officers resulted in the elections for the year 1926 as follows:

For President;	Dayton C. Miller
For Vice-President;	K. T. Compton
For Secretary;	Harold W. Webb
For Treasurer;	George B. Pegram
For Members of the Council, Four-year term;	A. H. Compton E. P. Lewis
For Managing Editor of the Physical Review, Three-year term;	John T. Tate
For Members of the Board of Editors of the Physical Review, Three-year term;	J. A. Gray G. E. M. Jauncey J. H. Van Vleck

The Secretary reported that during the year there had been 171 elections to membership, and that the resignations of 54 had been received. The deaths of 5 members were reported during the year. The total membership was 523 Fellows, and 1237 Members, making a total of 1760.

The Treasurer presented his financial report for the year 1925. The Managing Editor of the Physical Review presented the financial report for the year 1925, together with a report showing the progress of the Review during the years 1923, 1924 and 1925.

On motion of Professor R. A. Millikan, the following resolution was unanimously passed:

"*Resolved* that the Physical Society express its appreciation to the retiring Editor of the Physical Review for the following specific reasons:

1. He has introduced an abstracting system which had proved a distinct contribution to bibliographic method and has made the Physical Review in this respect a model already followed by many journals.

2. He has greatly improved the quality of the papers appearing in the Review, by an immense amount of detailed editorial work, and by insisting that contributors present their results with brevity and elegance.

3. He has given a demonstration of value to other sciences in that a journal, which a few years ago seemed unable to run without a subsidy, has been made to do so by attention to brevity and other elements of quality. By these services Dr. Fulcher has made an outstanding contribution to scientific progress."

Meeting of the Council.—At the Meeting of the Council held on December 28, 1925, three persons were elected to Fellowship, one was transferred from Membership to Fellowship, and twenty-six were elected to

Membership. *Elected to Fellowship:* William Bowie, Otto Laporte, H. Nagaoka. *Transferred from Membership to Fellowship:* Kanji Honda. *Elected to Membership:* Penrose S. Albright, Edward V. Appleton, Z. T. Chang, James L. Dunham, H. F. Fruth, R. J. Havighurst, Leland D. Hemenway, Victor Henri, Edward L. Hill, H. J. C. Ireton, Z. N. Loh, Daniel P. Mahoney, Roy H. Mortimer, Suminosuke Ono, Robert H. Oster, Neil B. Reynolds, Carl S. Roys, Richard Rudy, Matthew H. Schrenk, Surain Singh, Hildegarde Strücklen, Clyde H. Tarney, Henry W. Taylor, Tillman G. Titus, Louis J. Waldbauer, Robert G. Wulff.

The regular program of the American Physical Society consisted of 53 papers, Numbers 11, 14, 16, 19, 23, 25, 26, 37, 38, 41, 44, 47, 51 and 52 being read by title. The abstracts of these papers are given in the following pages. An **Author Index** will be found at the end.

HAROLD W. WEBB,
Secretary.

ABSTRACTS OF PAPERS

1. A correspondence theorem for the Compton effect. G. BREIT, Carnegie Institution of Washington.—As has been discovered by Bohr, the frequency emitted by a hydrogen atom as it falls from one of its quantized states to another may be expressed as a properly taken average of the frequency of the electron in its orbit (or of an overtone of that frequency) between the initial and the final state. In the present paper it is shown that the same is true for the Compton effect. The frequency actually scattered is a properly taken average of the frequency which would be scattered on the classical theory as the electron is accelerated from its state of rest to its final recoil condition. Similarly, the intensity scattered in various directions may be represented as a proper average of the intensities scattered on the classical theory. This point of view eliminates the difficulty of a constant correction-factor which has been encountered by Compton and Woo in their explanation of intensity relations.

2. Experimental values on the ratio of the modified to the total scattering of x-rays. O. K. DE FOE, Washington University.—Using the null method described at the Chicago meeting of the Physical Society for measuring the ratio of the modified scattering coefficient s_2, to the total scattering coefficient (s_1+s_2), a determination has been made for copper and carbon. The wave-lengths used ranged from .2A to .7A while the scattering angle was varied from 60° to 120°. The experimental values of $s_2/(s_1+s_2)$ appear to be always less than the values of this ratio as calculated from Jauncey's theory (Phys. Rev., **25**, 314 and 723, 1925), thus agreeing with the result reported by Woo at the Chicago meeting. Further experiments are in progress for the scattering from other substances. It may further be remarked that the rate of decrease of the experimental values of the ratio of $s_2/(s_1+s_2)$ is greater than the rate of change in the theoretical ratio. A possible interpretation of this is that the probability of scattering by an electron depends upon whether or not the difference in energy between the primary and scattered quanta is sufficient to eject the electron from the atom.

3. An experimental test of the Raman and Ramanathan theory of the diffraction of x-rays by liquids. E. H. COLLINS, University of Iowa.—The liquids, ether, water and glycerine were inclosed in small, thin walled glass cylinders at the center of the x-ray spectrometer and the diffraction curve—intensity of diffracted x-rays plotted against angle from incident beam—was determined by means of an ionization chamber and electrometer and compared with theoretical curves plotted from a formula given by Raman and Ramanathan. Raman and Ramanathan suggest that ether, because of its high compressibility, should give a broad peak in the diffraction curve. The experimental curve is found to have a broad peak. However, the theoretical curve plotted from their formula is found to be sharp due to the fact that the mean molecular distance is found experimentally to be large. The curves for water and glycerine show closer agreement but there is no evidence of the uniqueness of the theory.

4. Photometric measurement of x-ray plates showing the L absorption of tungsten. C. B. Crofutt, University of Arkansas.—In previous work (Phys. Rev. **24**, 9, 1924) both the absorption and emission spectra of tungsten were photographed simultaneously on the same plate. It has since seemed advisable to make a photometric analysis of the plates showing the absorption bands. The present paper contains an account of this work and includes the photometric curves obtained in the region of the three L absorption bands. The results are in agreement with the previous results. This work was done at the University of Iowa.

5. The intensity of reflection of x-rays by powdered sodium chloride. R. J. Havighurst, National Research Fellow, Harvard University.—The relative intensities of reflection of the Mo Kα doublet from most of the planes between (111) and (8,6,2-10, 2,0) of powdered NaCl have been measured with an ionization spectrometer, using the focusing method of W. H. Bragg, Brentano, Owen and Preston. The powder was pressed into the form of a thin briquet, and adjusted on the crystal table so that the relation $a/b = \sin\alpha/\sin\beta$ was always satisfied, where a and b are the distances from center of crystal table to focal spot and ionization chamber slit respectively; α is the angle between the primary beam and the surface of the briquet and $\beta=2\theta-\alpha$, where 2θ is the total deviation. The NaCl particles had an average diameter of 8×10^{-5} cm, so small that the effect of extinction (Darwin, Phil. Mag. **43**, 800, 1922) is negligible. The experimental values of the relative intensities were substituted in the equation given by Darwin and A. H. Compton for intensity of reflection and values of $f^2 e^{-b\sin^2\theta/\lambda^2}$ as a function of the distance between planes and of the electron distribution in the atoms, obtained for different values of θ. These values are in fair agreement with those of W. L. Bragg, James and Bosanquet (Phil. Mag. **42**, 1, 1921) obtained from single crystals of rock-salt, after the application to the latter of a correction for secondary extinction.

6. Secondary electrons from iron; critical potentials. H. E. Farnsworth, University of Maine.—The magnitude of the secondary electron current from Fe was measured as a function of the primary accelerating potential, 0 to 300 volts. Limiting curves were obtained for two different specimens of Fe after red-heat treatment and for a film of Fe deposited by evaporation. Three different forms of apparatus were used. In all cases the curves show sharp maxima at 1.2 and 7.0 volts with minima at 3.7 and 9.0 volts, and a less sharp maxima and minima at 10.0 and 12.0 volts, respectively. A steady upward trend of the curve begins at 12.0 volts, which is interpreted as an ionization potential. Potentials corresponding to the position of the maxima are interpreted as resonance potentials. Attempts to locate higher critical potentials than the above showed that the positions of slight changes in slope of the curve varied with uncontrollable conditions and with form of apparatus used. These slight changes are taken to have no real significance. Disagreement between these results and those of other observers is mentioned. While previous results for Cu indicate that a layer deposited by evaporation is amorphous, the present results indicate that a similarly formed layer of Fe is crystalline. These experiments were performed at University of Wisconsin last summer.

7. Voltage-intensity relations of mercury lines below ionization. D. R. White and Harold W. Webb, Columbia University.—Using a special four-electrode tube (hot cathode and three grids) voltage-intensity curves have been obtained in mercury vapor for about twenty lines in the wave-length interval 2500-5800A. The voltage-intensity relationship for each line appears to be primarily a function of the outer energy level involved. This is very clearly shown by two pairs of lines 4358 ($2p_2-1s$), 5461 ($2p_1-1s$) and 2893 ($2p_2-2s$), 3341 ($2p_1-2s$), each pair of which gave voltage-intensity curves practically identical in form. The groups of lines starting at the $3D$, $3d$ and $4D$, $4d$ levels show similarities, though not as marked. Abrupt changes of slope are to be observed in the curves which seemingly correspond to certain critical potentials. The voltages at which the lines first appear agree with theory, as in previous work by Eldridge and by Hertz.

8. Fine structure of the Balmer lines. WILLIAM V. HOUSTON, National Research Fellow, California Institute of Technology.—A Fabry-Perot interferometer can be used to measure these doublets without the usual errors due to overlapping of the components, if the plate separation is so adjusted that the weaker component comes in the middle of the space between adjacent orders of the stronger component. In this way $H\alpha$ is found to have a wave-number separation of about .31, while $H\beta$ has a separation of about .33. The resolution is such that the difference between these two can be seen by a casual examination of the plates. This is explicable on the theory of Sommerfeld, if it is assumed that the field within the tube is sufficient to suspend the principle of choice and to cause the appearance of those lines corresponding to a change of zero in the azimuthal quantum number. If this is true, the short wave-length component of $H\alpha$ should be a doublet with a separation of about .05A. While this has not yet been resolved, the line on many plates looks like a close doublet, and further examination will be made with a microphotometer.

9. Duration of radiation excited in hydrogen by 10.2-volt electron impacts. F. G SLACK and HAROLD W. WEBB.—Using the method already described (Phys. Rev. **24**, 113, 1924) in which high frequency voltages are applied in phase to the grids of the excitation and photo-electric systems of a four-electrode tube, the life of the $2P$ state in hydrogen, excited by 10.2-volt electron impacts was measured. Excitation was produced only in the positive half-cycle and the peak voltage was too low to permit other than the 10.2 radiation. It is improbable that absorption and re-radiation played any part due to the limited amount of dissociated hydrogen. The experimental curve agrees well with that calculated on the assumption that starting at the instant of impact the radiation falls off exponentially. The exponential constant found was $.83\times10^8$ sec.$^{-1}$ Unless the form of these curves is the result of a lag in the photo-electric effect, as seems improbable, the average time τ for an atom lifted to the $2P$ state by electron impact to return to its normal state by the process of emitting $\lambda1215.6$ is 1.2×10^{-8} seconds. If the photo-electric lag is effective this is the maximum value of τ. The same results were found for tubes of different dimensions and for pressures from .075 mm to .25 mm.

10. The time interval between the appearance of certain spectrum lines in the visible region. J. W. BEAMS, National Research Fellow, University of Virginia.—The experimental method consisted essentially in a comparison of the time interval elapsing between the appearance of two spectrum lines with the time required for light to travel a measured distance. The spectra of cadmium, zinc and magnesium in the spark in air and the spectrum of hydrogen in condensed discharges at various pressures were studied. The time intervals measured are as follows: In the spectrum of cadmium from the spark doublet 5378,38 to the line 4800 the time interval was 12×10^{-8} sec.; from 4800 to 5086, 1.3×10^{-8} sec.; and from 5086 to 4678, 0.7×10^{-8} sec. In the spectrum of zinc from the spark doublet 4924, 12 to the line 4680 it was 15×10^{-8} sec.; from 4680 to 4722, 2×10^{-8} sec.; and from 4722 to 4811, 1.3×10^{-8} sec. In the spectrum of magnesium, from the spark doublet 4481 to the triplet 5184, 73, 67 it was 8.2×10^{-8} sec. From 4481 of Mg to 5378, 37 of Cd it was 7.5×10^{-8} sec., and from 5378, 37 of Cd to 4924, 12 of Zn, 9.6×10^{-8} sec. In the spectrum of hydrogen, Hβ appeared first, Hγ second and Hα third.

11. The time interval between excitation and emission for fluorescein. L. G. Hoxton and J. W. Beams, National Research Fellow, University of Virginia.—Solutions of fluorescein at concentrations of 2.5×10^{-5} gm per cc were investigated. The exciting light was limited to the spark lines 4481 of magnesium. It was found that the time elapsing between the beginning of incidence and the beginning of fluorescent emission was $(3.2\pm0.3)\times10^{-8}$ sec. for the aqueous solution and $(3.7\pm0.4)\times10^{-8}$ sec. for the alcoholic solution. In the experimental method about half of the beam of exciting light was intercepted by the solution, the other half passing on and returning, after reflections, by a path whose length could be varied, to a point close enough to the point of division to be seen in the same field as the fluorescent light through an optical system (a modification of the arrangement of Abraham and Lemoine) which was, in effect, a shutter electrically operated by the spark discharge. Its time of closing was advanced until the fluorescent light just disappeared from view; then the light path was lengthened until the returning light did likewise. The time interval sought was thus made equal to that required for light to travel a measured distance.

12. Band series in infra-red absorption spectra of organic compounds. Joseph W. Ellis, University of California, Southern Branch.—A series of outstanding absorption bands below 3μ, already attributed to a carbon-hydrogen bond, is shown to fit accurately the non-linear equation, $\nu_n\times10^{-12}=47.37n-0.783n^2$, (1), where ν_n is the frequency and $n=3, 4, 5$, etc. Numerous secondary absorption maxima in the spectra of both the open chain and closed ring types of compounds, containing only carbon and hydrogen atoms, fit the linear equation, $\nu_m'\times10^{-12}=10.71m$, (2), where $m=10, 11, 12$, etc. They are attributed to a carbon-carbon linkage. All other short wave-length bands can be accounted for by simple additive combinations of low frequency members of series (1) and (2), $\nu_c=\nu_n+\nu_m'$. Other members of these three series are identified in longer wave-length spectra obtained by Coblentz and other investigators.

13. The quantum analysis of the rotational energy of certain molecules. Raymond T. Birge, University of California.—The formulas recently derived for the constants of the molecular law of force enable one to calculate, from data on a set of *vibrational* states, the higher order terms of the *rotational* energy function. This must be assumed an even-powered function of the nuclear momentum m. The rotational energy data may thus be reduced to a theoretically linear equation whose two constants give the most probable values of the moment of inertia I_0 and electronic momentum ϵ. This method was suggested to the writer by E. C. Kemble. The results in the case of CuH give evidence in favor of half-integers for the *resultant* momentum of the molecule, and for the initial excited state alone, require a small value of ϵ (0.0059), which *increases* with m. The variation in ϵ is due presumably to the warping of the electron orbits, caused by the nuclear rotation. This new method uses all of the data, in determining I_0 and ϵ, and to this fact is due its great accuracy. Separate papers give the results in the case of the Swan bands and the AlO bands. In *all* cases the resultant electronic momentum and nuclear momentum are parallel and in the same sense.

14. Molecular constants determined from the Swan bands. J. D. Shea and R. T. Birge, University of California.—Using the method recently developed for obtaining accurate values of the moment of inertia I_0 and electronic momentum ϵ of certain types of molecules, the following results have been obtained for the rotational energy F (in wave-numbers) of the non-vibrating molecule. For the initial state $F=1.7541m^2-6.911\times10^{-6}m^4+1.22\times10^{-11}m^6$, where $m=k-\epsilon=k-(0.0989+1.746\times10^{-5}k^2)$. k is a half-integer and represents the *resultant* molecular momentum. Hence $I_0=15.792\times10^{-40}$.

For the final state $F=1.6295m^2-6.594\times10^{-6}m^4+1.73\times10^{-11}m^6$, where $m=k-(0.0741+0.964\times10^{-5}k^2)$. Hence $I_0=17.000\times10^{-40}$. These constants have been obtained from the middle component of the triplets of the Swan bands. The values of I_0 and ϵ are surprisingly similar to those for the second positive group of nitrogen (known to be due to N_2) and since the HC·CH molecule has the same number of electrons and nearly the same mass as N_2, this *may* be the emitter of the Swan bands, if such a molecule can vibrate and rotate like a dipole. The above values of I_0 should be accurate to 0.10 percent, and replace the previous approximate values (Phys. Rev. **25**, 716, 1925).

15. The combination relation in the λ3064 OH band. WILLIAM W. WATSON, University of Chicago.—The P,Q,R combination which holds for any normal band is not satisfied in the MgH and OH bands, the defect being as great as 34 cm^{-1} at $m=22$ in the 3064 OH band. New measurements have been made on this band, and satellites of the Q lines have been located which, when combined with the main P and R lines, give the required combination. As predicted by Dieke, these satellites are found to be farther from the main lines than those reported by Fortrat. The possible rotational energy levels are considered.

16. Spectroscopic investigation of acetylene, methane and ethylene. FRANK C. MCDONALD, University of Chicago, (introduced by Harvey B. Lemon).—Although an attempt to obtain emission spectra from acetylene, methane and ethylene (in tubes of the Wood type, in tubes using an oxy-cathode, and in mixtures with helium subjected to a wide variety of pressures and methods of excitation) have failed to reveal any bands definitely ascribed to these complete molecules, a new band spectrum has been observed when methane, in a Wood tube, at a pressure of about 2 mm, is excited by a violent disruptive discharge. This spectrum consists of three bands degraded to the red, with heads at 2263, 2367, and 2395A. Their location where the dispersion of the quartz spectrograph is large and their open character make possible a study of their fine structure, which is now in progress and which it is hoped will reveal their relation to other hydrocarbon spectra. Methane and ethylene in tubes 150 cm long with quartz ends, at pressures up to 90 cm show no absorption, while the absorption of acetylene begins at shorter wave-lengths than that reported by Henri.

17. "True half breadth" of absorption lines. THOMAS M. DAHM, University of Idaho.—True half breadth is discussed by Harrison and Slater. (Phys. Rev. **26**, 176, 1925, and **25**, 783, 1925.) While the shape of the T (transmittancy) curve varies with x, the shape of the $\log_e\log_e(1/T)$ curve is independent of x. For infinitesimal x, $\log_e\log_e(1/T)=\log_e(1-T)=\log_e$ (absorption). Hence "true half breadth" may be obtained by measuring the length of horizontal line drawn at distance $\log_e 2$ below crest of $\log_e\log_e(1/T)$ curve, provided there is no general absorption. If k_0, k_1 and k_2 are absorption coefficients at λ_0, λ_1 and λ_2, where $\lambda_2-\lambda_0=2(\lambda_1-\lambda_0)$, $k_0(4k_2-k_1)-3k_1k_2=0$, with no general absorption, assuming Slater's Eq. (9). $K_0(4K_2-K_1)-3K_1K_2=\Delta$, if there is constant general absorption. Reducing each experimentally determined K by amount $K^1=\Delta/(3K_0-4K_1+K_2)$ corrects for general absorption. A new curve of $\log_e\log_e(1/T)$, or of $\log_e k$ which has the same shape, may be plotted and the "half breadth" found graphically, as above. k^1 need not be found by trial as in Slater's method, and C_1C_2 is determined directly from the curve. If general absorption is variable, of amount k^1, k^1+a, k^1+2a, at λ_0, λ_1, λ_2, $k^1=\Delta-a(7K_0-6K_1-3K_2+6a)/(3K_0-4K_1+K_2+2a)$, a being determined by trial, provided it is small enough not to displace λ_0 too much.

18. The absorption spectra of the vapors of aluminum, gallium, indium and thallium in the ultra-violet. JOHN G. FRAYNE, Antioch College, and ALPHEUS W. SMITH, Ohio State University.—(1) *Absorption in heated vapors.* The metals were vaporized in a graphite tube 15 cm long heated with an oxy-acetylene torch to 2000°C. A tungsten under-water spark provided a continuous spectrum. *Aluminum.* At about 1200°C the first seven pairs of the first subordinate series were absorbed. The relative intensities disagree with the Bohr theory. No absorption was observed for the second subordinate series. *Gallium.* At a temperature of about 1500°C, 17 prominent lines appeared, including the first four pairs of the first and second subordinate series and the 5th term of the $2p_1-ms$ series. *Indium.* At about 1200°C 18 lines appeared, including the first three pairs of the first subordinate series, the first 5 pairs of the second subordinate series and the 4th term of the $2p_1-md$ series. *Thallium.* At 400°C 4 lines of the $2p_2-ms$ and 4 of the $2p_2-md$ series appeared, widening into bands with increasing temperature. At 800°C lines from the $2p_1$ level appeared as fine absorption lines. (2) *Absorption in the arc.* A bead of the metal was placed in the crater. *Aluminum.* In a 15 amp. arc the lines of the $2p_2-md$ and $2p_1-md$ series, $m=5$ to 11 were completely absorbed. *Indium.* The lines $2p_2-2s$, $2p_2-3d$, $2p_1-2s$ and $2p_1-3d$ were completely absorbed.

19. Interference in a spectrometer with white light and wide slit. H. M. Reese and L. E. Pinney, University of Missouri.—The ring-pattern from a Fabry-Perot interferometer is focussed upon the slit of a non-astigmatic concave grating spectrometer. With illumination in white light, a series of curved interference fringes is found, as expected, in the focal surface of the spectrometer. It was observed, however, that although the fringes disappear when the slit is widened a little, they reappear if the widening is continued. For slit-widths ranging from zero to 1.5 or 2 mm, 9 or 10 disappearances and reappearances of the fringes can be observed in the green region, and more at shorter wave-lengths. A theory of the phenomenon, involving some approximations, is presented and shown to be in quantitative agreement with the observations.

20. Optical constants of single crystal bismuth. L. H. Rowse, University of Iowa, (introduced by E. P. T. Tyndall).—The index of refraction and extinction modulus for light traveling parallel to the optic axis were determined by measuring the ellipticity produced by reflection from the cleavage surface of single crystal bismuth. A Stokes analyser was used and readings were taken in the visible spectrum only. The index of refraction rises from 1.05 at 470 $m\mu$ to 1.55 at 670 $m\mu$, while the extinction modulus rises from 2.7 at 470 $m\mu$ to 3.6 at 670 $m\mu$. The computed reflectivity lies between 65 and 70 percent. The results are compared with those of other observers made on polished surfaces.

21. Optical constants of molybdenite in the ultra-violet. Alfred W. Meyer, University of Iowa, (introduced by E. P. T. Tyndall).—The index of refraction and extinction index for light transmitted parallel to the optic axis in crystals of molybdenite were determined by measurements of the ellipticity produced by reflection at a cleavage surface. Minor's method was used. The index of refraction rises to a maximum of 7.8 at 480 $m\mu$ and falls to 2.7 at 330 $m\mu$. The extinction index rises steadily from 0.35 at 500 $m\mu$ to 1.0 at 360 $m\mu$ and remains constant to 330 $m\mu$. The reflectivity is computed and compared with results of other observers.

22. Luminescence of Grignard compounds in magnetic and electric fields. R. T. Dufford, Dorothy Nightingale, and L. W. Gaddum, University of Missouri.—The writers in co-operation with several other workers, have investigated the effects of electric and magnetic fields on the luminescence of organo-magnesium halides in ether solutions. In magnetic fields of the order of 15,000 gauss, the luminescence due to oxidation in air or oxygen is found to be notably brighter in the more intense part of the field. Polarization of the light appears to be nearly if not completely absent. It is impossible to apply large electric fields, on account of the abnormally large conductivity of such solutions. With voltages up to 1500, it is found that the compounds that give luminescence on oxidation with O_2 give light at the anode, but the brightness is not in the same order as with O_2. Polarization appears to be absent here also.

23. On the spectroscopic examination of the striated discharge in mixed gases. David A. Keys and M. Home, McGill University.—Continuation of the work on the striated discharge in hydrogen (Trans. Roy. Soc. Canada, **19**, 143, 1925) using the same apparatus but mixtures of (1) hydrogen with helium and (2) hydrogen with nitrogen gave the following results. In the mixture of helium and hydrogen, the Hα line is hardly visible in the negative glow but strong in the striation. The Hβ line, however, is easily visible in the negative glow, i.e., its intensity is stronger than Hα, but in the striation it is weaker than Hα. With a mixture of nitrogen and hydrogen, the Hα and Hβ lines are strong in the negative glow but not detectable in the striation. This is the reverse of what was found in helium and hydrogen. When only hydrogen is used, the Hα and Hβ lines are stronger in the negative glow than in a striation.

24. Resonance potentials in gallium and indium vapors. C. W. Jarvis, Ohio Wesleyan University, (introduced by Alpheus W. Smith).—The critical potentials of gallium and indium were investigated by the methods of inelastic impact. The tube containing the vapors was the differential type used by Hertz but so arranged that by making the proper electrical connections it could be used as a simple three-electrode tube. The three following methods were employed to detect direct ionization: (1) the change of the negative space charge, (2) the Lenard method, (3) the modification of the gap resistance. The results obtained for gallium are: (1) 3.06 ± .05 volts. This resonance potential corresponds to λ4033 A and the transition $2p_2-2s$. (2) 4.22 ± .05 volts which corresponds to λ2874 A and the transition $2p_2-3d_2$. In gallium there was evidence of weak ionization at about 6 volts and a stronger second ionization at about 13 volts. Two resonance potentials were also observed for indium. They are as follows: (1) 3.03 ± .05 volts corresponding to λ4102 A and the transition $2p_2-2s$. (2) 4.07 ±05 volts corresponding to λ3039 A and the transition $2\ p_2-3d_2$. In indium as in the case of gallium there was evidence of weak ionization at about 6 volts and a stronger second ionization at about 14 volts. The failure to get satisfactory ionization for these metals at the voltage corresponding to the first ionization potential is attributed to the small vapor pressure at the temperature used in these experiments, namely 500° to 600° C.

25. Low voltage arcs in iodine. H. F. Fruth and O. S. Duffendack, University of Michigan.—Low voltage arcs in monatomic and molecular iodine were investigated together with their spectra. From a study of the current-voltage characteristics it was concluded that 6.5 volts is the minimum radiating potential of the atom, 8.0 the ionizing potential of the atom, and 9.5 the ionizing potential of the molecule. Non-oscillating abnormal low voltage arcs were maintained down to 4.9 volts and oscillations were observed around 12 volts. With arc currents of about 2 amperes the filament current could be cut off and the arc sustained indefinitely at 30 volts or above. The spectrum of the 4.9 volt arc contained only 3 lines, (λλ2062, 2535, 3135) the continuous band 3460, and several groups of bands. At slightly higher voltages arc lines appear and at 8 volts the strongest spark lines begin. These lines are succeeded by new ones at higher voltages making it seem probable that the stripping of the atom is in progress. Peculiar behavior of the lines 2535 and 3135A was observed. Three continuous bands (at 4080, 4300, 4800A) are present in molecular but disappear in atomic iodine. A band system lying between 2224 and 2050A was observed, and two groups of four bands each were found at 2880, 2833, 2776, 2716A and 2480, 2379, 2290, and 2243A.

26. The magnetic properties of atomic rays of the alkali metals. John B. Taylor, University of Illinois, (introduced by Jacob Kunz).—The direct experiments of Gerlach and Stern on space quantization with atomic rays of silver, have been repeated in a simplified apparatus. A broadening of the atom stream was found, rather than the actual splitting which Gerlach and Stern were able to detect. The splitting would probably be obtained with narrower slits. Work is now in progress on the alkali metals.

In order to insure deposition of the alkali metal to form an image of the slit, it is necessary to cool the plate with liquid air. Preliminary results on sodium indicate a broadening of the image by a magnetic field as in the case of silver, but the effect obtained so far is too small to establish the conclusion beyond doubt

27. Conductivity of activated nitrogen. Philip A. Constantinides, University of Chicago, (introduced by H. B. Lemon).—The conductivity in activated nitrogen produced by an electrodless discharge has been directly measured. Nitrogen gas moving with a uniform velocity has been activated in a bulb, and then passed in an ion chamber consisting of a metal tube charged to suitable potentials with respect to an electrode along its axis connected to an electrometer. The ion current when plotted as a function of the cylinder potential follows Ohm's law to the neighborhood of saturation potential. By increasing the potential beyond the saturation potential an increase of ion current is observed in the vicinity of the ionization potential of N_2.

28. Theory of the cathode of an arc. J. J. Slepian, Westinghouse Research Laboratory, East Pittsburgh.—It is generally believed that thermionic emission at the cathode is essential for the maintenance of an arc, although a number of serious objections have been raised against this view. K. T. Compton has explained the conductivity of the positive column in an arc by thermal ionization of the gas. The author shows that this hypothesis of thermal ionization of the gas may also explain the passage of current to the cathode so that liberation of electrons from the cathode is not necessary, the current being carried to the cathode by positive ions. Quantitative calculations by equations of Saha and Langmuir give reasonable values for the temperature of the gas.

29. The positive ion emission from a mixture containing Fe, Al and Cs, and the work function φ_+ for Cs from this mixture. C. H. Kunsman, Fixed Nitrogen Research Laboratory, U. S. Department of Agriculture.—A mixture consisting of magnetite to which about 1% of Al-oxide and about ½% Cs in the form of caesium nitrate was fused in a resistance furnace, where the material itself was the resistor. This mixture furnished a very definite source of positive ions when used as a hot anode in a vacuum. The magnitude of the ion current depended upon the previous gas treatment and state of reduction of the material. After a thorough degassing and glowing in a vacuum, the positive ion current was sufficiently constant at a given temperature so that a very definite and reproducible value of the work function, $\varphi_+ = 2.37$ volts, was obtained by means of Richardson's equation $I_+ = AT^{\frac{1}{2}}\epsilon^{-\varphi e/kT}$ for temperatures from 962° to 1185°K. That this emission was largely positively charged ions of Cs was determined by the electron emission characteristics of a tungsten filament, placed so as to collect some of the positively charged particles. The reduced mixture of the oxides of Fe, Al and Cs is a good catalyst for the synthesis of ammonia from N_2 and H_2.

30. Departures from Ohm's law and theories of metallic conduction. K. T. Compton, Princeton University.—Four years ago Bridgman reported departures from Ohm's law of the order of one percent for current densities of the order of 10^6 amp. per cm^2 in gold and silver. It is shown that such departures render untenable Thomson's "second" (or doublet) theory of conduction, but are of the order to be expected on the classical free electron theory. The classical electron theory expression for conductivity is used, except that account is taken of the fact that the electrons are not in thermal equilibrium with the atoms but have greater energies on account of the field. These energies are calculated after the manner of "terminal" energies. The electronic free path can be calculated from the experimental data by

$$l = (\alpha T/Ee)[(9.072m/M)(\sigma - \sigma')/\sigma]^{\frac{1}{2}}$$

where σ and σ' are the conductivities at low current density and with potential gradient E, respectively, m and M are electronic and atomic masses and αT is the mean kinetic energy of the atoms. The free path l comes out $2.85(10)^{-6}$ cm for gold, a value consistent with other indications. Critical experimental tests of the theory are suggested by the equations.

31. The resistivity of liquid alloys. C. V. Kent, Kansas University.—The expression $\rho = 2mW/Ne^2$ for the resistivity ρ of a metal (W being the free electron impact frequency and N the free electron density) in the simple electron theory, is consistent with electrical and optical data for molten metals and alloys (C. V. Kent, Phys. Rev. **14**, 459, 1919, and **23**, 479, 1923). W and N seem to be linear functions of the atomic or molecular percent of one component in the alloy, or of one component in the component-compound alloy when such compound (or aggregate) is indicated by the melting point diagrams. The atomic concentration-resistivity graph should then be one or more sections of rectangular hyperbolae. This conclusion has been tested from the data of others and for some obtained by Mr. Geo. Emery and the writer, and is apparently confirmed. Furthermore the free electron concentration is independent of the temperature, the entire temperature change in resistivity being due to the variation in the free electron impact frequency with the temperature. The data available are generally insufficient and further experimental work is in progress. There is some evidence that the resistivity curves of some solid alloys obey the same laws.

32. The location of the electromotive forces in galvanic cells and thermocouples. W. H. Rodebush, University of Illinois.—Electromotive forces may be classified as (1) electromagnetic, (2) electrostatic, (3) electrokinetic. In the galvanic cell the conclusion is drawn that the principal e.m.f. resides at the junction of electrode and solution. There is neither an e.m.f. nor a difference of potential of appreciable magnitude at the metallic junctions. In the thermocouple the e.m.fs. are electrokinetic. The second law of thermodynamics does not indicate the location of these e.m.fs. but the first law requires them to be associated with heat effects. In a thermocouple with infinitesimal temperature difference between junctions these e.m.fs. are to be referred to the junctions. This conclusion can be extended to cases where a finite temperature difference exists.

33. Experiments with standing electromagnetic waves produced by means of a short wave electron tube oscillator. Alexander Marcus, College of the City of New York.—For laboratory experiments with electric waves about two meters in length, the following type of short-wave generator has been found convenient. A linear oscillator adjustable to a length of about one meter is energized by means of an oscillating circuit consisting of a single turn of wire about four inches in diameter, with its ends connected to the grid and plate respectively of an ordinary electron tube like the 201A type. The wire is broken at its midpoint and a variable condenser having a maximum capacity of 0.0001 mf is inserted for the purpose of facilitating the tuning of the closed driving circuit to the fundamental wave-length of the linear oscillator. The latter has a hot-wire meter at its center to indicate the production of a current antinode at resonance. The polarized waves radiated by the linear oscillator may be conveniently detected by means of a similar linear oscillator with a thermal galvanometer inserted at its middle point. With the help of a grid of several parallel wires it is easy to produce standing waves having prominent nodes and loops in a room of ordinary size. A pair of Lecher wires loosely coupled to the driving circuit affords a check method of measuring the wave-length.

34. Application of a vacuum tube multimeter to electrical measurements at radio frequencies. S. Leroy Brown and M. Y. Colby, University of Texas.—The usual low frequency voltmeter-ammeter methods of measurements can be extended to include audio and radio frequencies by the use of a vacuum tube meter utilizing two triodes. The grid potential of the first tube is lowered proportionally to the peak value of the applied voltage; this decreases the plate current of the first tube and the direct potential drop across a high resistance in its plate circuit is so applied in the grid circuit of the second tube that the result is an increase in the plate current of the second tube which is measured by a direct current micro-ammeter. This instrument is so constructed that its input impedance is very high, it is independent of the nature of circuit to which it is connected and its registration is independent of frequency up to a million cycles per second. The lowest measurable electromotive force is about .05 volts and, therefore, with a non-inductive resistance of 1000 ohms, a current of 50 micro-amperes can be measured. Other applications of the instrument are: testing of audio and radio transformers, measurement of induced electromotive force in loop aerials and the intensity of harmonics, and the detecting of bridge balance.

35. Accurate measurement of small capacities. William Schriever, University of Oklahoma.—The capacity of an electrometer and its connections may be obtained by the usual condensers-in-parallel method but the results will not be accurate unless the capacity of the shielded connecting wire is taken into account. By connecting each of two cylindrical condensers (alike in every respect except length) to the electrometer system in exactly the same way, it is possible to eliminate the "end-effects" in the calculations. These "end-effects" include the errors due to the finite length of the condensers (formula for capacity of concentric cylinders per unit length assumes them to be of infinite length), the errors due to the presence of insulating material between the parts of each condenser, and the errors due to the capacity of the wire connecting the condensers to the electrometer system. A constant source of ionization is required.

36. Measurement of the high frequency resistance of coils. R. R. Ramsey, Indiana University.—The high frequency resistance of a coil is measured by comparing the heat (I^2R losses) produced in the coil by a radio frequency current (10^6 cycles) to the heat produced by a d.c. current in a known resistance. A differential thermometer is made of two inverted Pyrex beakers cemented to glass plates. Through each glass plate two electrical connections and a glass tube are cemented. The glass tubes are connected to a U-tube half filled with water. The coil to be measured is placed in one beaker and the known d.c. resistance is placed in the other. The heat developed in the two coils as indicated by the water in the U-tube is made equal by varying the d.c. current. The high frequency resistance of the coil is found to be less than that found by measuring the resistance of the circuit by the usual method in which the resistance of the condenser is assumed to be negligibly small. With a constant frequency the difference increases with the inductance of the coil.

37. The variation of the resistance of condensers with dial setting at radio frequencies. A. E. Maibauer and T. Smith Taylor, Bakelite Corporation.—In the measurement of the power factor of insulating materials by the resistance variation method, or by the substitution method, it has been customary to consider the resistance of the standard condenser as negligible compared with that of the sample under test. The writers were aware of the fact that this assumption was not justified and have determined the values of the effective series resistance of two condensers used as standards in power factor measurements. Use was made of a standard condenser made from two adjustable parallel plates. This condenser having either nothing but air, or very small pieces of Pyrex glass or mica as dielectric had as small an effective resistance at 1,000,000 cycles as it was possible to obtain. Curves are given which show how the resistances of condensers vary with dial settings.

38. A new type of electromagnetic wave-meter. W. W. Salisbury, University of Iowa, (introduced by C. J. Lapp).—A high degree of accuracy and sensitivity are obtained by using a combination of a two element vacuum tube and direct current galvanometer, which measures the voltage across the condenser in the resonant circuit instead of the current in the inductance as is the common practice. The small amount of energy necessary to operate this indicator makes possible a very sharp resonance peak. Its sensitivity allows it to be operated so far from the source of the waves that it does not effect the wave-length. A new method of locating nodes on Lecher's wires makes possible greater accuracy than has previously been obtained in such measurements. The wave-meter is calibrated, with the aid of these wires, for wave-lengths between 3 and 100 meters.

39. An electrical frequency meter of wide range. HOMER L. DODGE, University of Oklahoma.—The paper describes a direct-reading, electrical frequency meter of wide range made up of standard electrical laboratory equipment consisting principally of condensers and an a.c. milliammeter.

40. Dielectric constant of helium and oxygen in a magnetic field. B. B. WEATHERBY and A. WOLF, University of Pennsylvania.—The heterodyne beat method was used to detect a possible change in the dielectric constant of gases, due to space quantization in a magnetic field. A condenser, forming a part of one oscillating circuit of about 1,000,000 cycles frequency, was filled with the gas investigated and the magnetic field then applied.. The results obtained show that for helium (20 cm pressure), air (76 cm) and oxygen (76 cm) at room temperature there is no change in the dielectric constant to 1 part in 500,000. The magnetic field was of the order of 8000-10,000 gausses, while the electric field was estimated at 5000-10,000 volts/cm. The tests were carried out with the direction of the electric field both parallel and normal to the direction of the magnetic field. This work was suggested by theoretical considerations in an article by Ruark and Breit (Phil. Mag. Feb. 1925).

41. Effect of deposition-temperature on the magnetic properties of evaporated nickel films. R. L. EDWARDS, University of Iowa.—Uniform nickel films of thickness $30m\mu$ to $300m\mu$ were produced by evaporation on an aluminum foil base. Deposition occurred at temperatures ranging up to 250°C with a vacuum in most cases better than .003 mm. The magnetic properties were quantitatively determined with fields up to 139 gauss. Films deposited on an unheated surface were found to be only slightly magnetic, but for such films, the coercive force was also very small. The effect of maintaining films at a relatively high temperature during deposition was to greatly increase the permeability for large fields, and to increase the coercivity in a still greater ratio—that is, to increase both dimensions of the hysteresis loops. Loops plotted on the same scale of magnetic induction and field strength varied in area more than ten-fold due to this cause. Areas more than eighteen times as great as for annealed bulk metal were obtained. Presumably the films were crystaline, and their formation on a heated surface would produce larger crystals, yet such films were harder physically as well as magnetically than those produced on unheated surfaces.

42. Thermo-electric power and the Hall coefficient. C. W. HEAPS, Rice Institute.—The simpler theories of free electrons in metals make the Hall coefficient depend only on electron concentration. The thermo-electric power of a couple depends on the ratio of electron concentrations in the two metals. A relation between Hall coefficient and thermo-electric power is thus to be expected. Experiments performed on Bi and Sb show a Hall coefficient decreasing as the magnetic field increases while the thermo-electric powers of these metals with respect to copper increase. For crystalline graphite, increasing the magnetic field increases the Hall coefficient and decreases the thermo-electric power. No other non-magnetic metals have been found to have a variable Hall coefficient or thermo-electric power (with the possible exception of Te) so the tentative rule may be stated: If the Hall coefficient of a non-magnetic metal varies with the field the thermo-electric power of that substance will be found to vary in a converse way with the field. Richardson has suggested that any cause producing a continuous alteration of electrical conductivity at a given temperature should produce a corresponding alteration of the thermo-electric power. A magnetic field acting on graphite does not appear to behave in accordance with this suggestion.

43. A "Node" at the source. G. W. Stewart, University of Iowa.—Current literature shows a fairly general misunderstanding concerning the nodal location of the vibrating source in the Kundt's tube and in the Melde transverse string and fork experiment. It is shown by theoretical deduction that this source is one-half wave-length from the nearest node, that it is located more correctly *at a node* than "near a node" or "practically at a node." Experimental justification is also cited. The motion of the source is the cause of the misunderstanding, but the source, a boundary between two media, has a displacement that is exceedingly small compared to a wave-length and reflects and permits stationary waves to form just as if it were stationary.

44. Measurement of air velocity by means of a Rayleigh disk. C. N. Wall, University of Illinois, (introduced by F. R. Watson).—A Rayleigh disk was suspended by means of a quartz fiber in a pipe through which flowed a uni-directional stream of air from a constant pressure tank. By independent measurements of the air velocity and the resulting torque exerted upon the Rayleigh disk an empirical relation between the two quantities was established. It was found that the torque exerted upon the disk by the air stream is proportional to the 1.7 power of the air velocity instead of to the square of the velocity as predicted by the classical theory.

45. The vapor pressure of solid potassium amalgams. Franklin E. Poindexter, Washington University.—A Buckley ionization gauge was used to measure the vapor pressure of three potassium amalgams ranging in concentration from 5 : 1 to 15 : 1 mol ratio of Hg to K. The vapor pressure of each amalgam was measured at a number of temperatures which were determined by means of a platinum resistance thermometer. The pressures measured varied from approximately 10^{-6} mm to 10^{-3} mm over a maximum temperature range of from $-24°$C to 28°C. The log p vs $1/T$ graphs for the different amalgams were found to be approximately straight lines. The heats of reaction were calculated by means of the Van't Hoff reaction isochore, the pressures at different temperatures for these calculations being taken from the log p vs $1/T$ graphs. These heats were of the order of 25,500 cal. per gram molecule of amalgam. The corresponding heats of reaction for sodium amalgams, as reported at the Chicago meeting of the Physical Society, were found to be of the order of 14,500 cal.

46. The relative importance of the Bernouilli principle and of viscosity in aspirator action. E. L. Harrington, University of Saskatchewan.—Although the Bernouilli principle is cited in most text books of physics as the complete explanation of aspirator action it is found from both theoretical considerations and experimental study that the viscosity of air is really by far the more important factor to be considered. Aspirators designed to more thoroughly utilize the latter are described and shown to be many times as efficient as those designed to utilize only the Bernouilli principle.

47. Measurements on the thermal expansion of fused silica. Wilmer Souder and Peter Hidnert, Bureau of Standards.—Expansion tests were made on transparent and non-transparent fused silica over various temperature ranges between $-125°$ and $+1000°$C. Seventeen samples of fused silica were examined on which a total of 48 expansion tests were made. A detailed description of the apparatus and the methods used in this research and a summary of available data obtained by previous observers on the thermal expansion of fused silica are given. A critical temperature or minimum length was found at about $-80°$C. Expansion occurred on heating fused silica above the critical temperature or on cooling below this temperature. Typical expansion curves are shown and discussed, and the authors' average expansion curve compared with the results of previous investigators. The following table gives average coefficients of expansion derived from the data on all samples for various temperature ranges.

Average Coefficients of Expansion per Degree Centigrade of Fused Silica.

20 to 60°C : 0.40×10^{-6}.
20 to 200 : .50;
20 to 400 : .55;
20 to 600°C : 0.53×10^{-6};
20 to 750 : .50;
20 to 1000 : .48.

48. **Piezo-electric effect in sodium bromate.** JOSEPH VALASEK, University of Minnesota.—The general problem of deduction of physical properties of crystals from their structure and kinds of atoms is a difficult one for which there may be some possible simplifications. Certainly, however, the replacement of the ions in sodium chlorate and bromate by point charges, leaves much of their piezo-electric moment unaccounted for. Experimentally, it is found that the change in the lattice constant of sodium bromate with temperature, which is given by the coefficient of thermal expansion, is 0.0000286, while the temperature coefficient of the piezo-electric constant is roughly one hundred times as large. This is entirely out of proportion to the change one would expect from a simple expansion of all atomic distances. By using different temperatures one can obtain the same piezo-electric constant from the sodium chlorate and bromate. This requires only a reduction of the bromate lattice by 10 percent of the difference between the two, that is, the bromate must be about 100°C cooler than the chlorate. The data show that the use of point charges instead of the ions in the crystal lattice cannot give correct results, and show the magnitude of the discrepancy. Details will be published later.

49. **Thermodynamics of thermionic phenomena.** N. RASHEVSKY, Westinghouse Research Laboratory, East Pittsburgh, (introduced by Dayton Ulrey).—An attempt is made to reduce all thermodynamical treatments of thermionic phenomena to the most general and exact form. In connection with this the kind of assumptions and approximations underlying all the thermodynamical methods used at the present time are investigated. Special attention is given to the rôle of the positive ions in the solid as well as in the gaseous phase and their possible mutual interaction with the electrons. Using the outlines of this general method, results obtained in a previous paper (Zeits. f. Phys. **33**, 606, 1925) as to the influence of pressure and the rôle played by the chemical constant of the emitter are confirmed, and furthermore are shown to be independent of the special assumptions made in that paper. In connection with a recent paper by W. Schottky the question is discussed as to whether the law of emission is the same for all substances or whether it may be different for elements and compounds.

50. **Simple demonstration of the constancy of mass.** J. A. ELDRIDGE, University of Iowa.—The content of the electromagnetic field equations is very nearly the same as that of restricted relativity. It is well known that many of the results of relativity were obtained much earlier by electromagnetic reasoning. The purpose of this paper is to show as simply as possible the variation of mass with speed and to make the mass concept more concrete. The relation between the charge and the Faraday tube of force is like that between a spider and its thread—the tube of force furnishes not only the accelerating force but also adds to the mass moved. The charge, if accelerated in the direction of its velocity, adds to itself a Faraday tube; a transverse (i.e. centripetal) acceleration means no accumulation of mass. These concepts give numerically the variation of mass with velocity and the difference between longitudinal and transverse mass. This picture of the diffuse stationary mass being absorbed by the denser moving mass is quite general and illustrates the general principle of conservation of mass.

51. An oscillographic study of atmospherics. Roy H. Mortimore, University of Iowa, (introduced by E. P. T. Tyndall).—The variations of potential accompanying lightning flashes induced current in a critically damped antenna. The potential across a series condenser in the antenna was amplified with a resistance coupled amplifier the output of which was connected to a Duddell oscillograph. The photographic records obtained show that the impulses are unidirectional, aperiodic, and vary in duration from 500 to 8000 micro-seconds.

52. The energy levels of the carbon monoxide molecule. Raymond T. Birge, University of California.—It is possible to arrange all of the fourth positive group of carbon, and also Lyman's "fifth positive group" and nearly all the remaining previously unassigned bands in one quantum system of some 150 bands, given by $\nu = 64{,}721 + (1499.28n' - 17.24n'^2) - (2147.74n'' - 12.703n''^2)$, where n' varies from 0 to 14, and n'' from 0 to 22. The distribution of intensity is a typical one, similar to that for the aluminum bands. The expected portion of these bands has been found by Leifson in absorption in cold carbon monoxide, and this system therefore represents the fundamental "resonance" system of CO. The Angstrom CO bands have as a final state the initial state of this same system. Duncan has unknowingly measured the excitation potential of the first negative group of carbon (due to CO^+), from which one obtains 14.2 volts for the ionization potential of CO. Therefore the relative energy values of three electronic levels for CO, and three for CO^+ are now known, and also the excitation potential for the fourth group of carbon (8.0 volts, "resonance potential"), Angstrom CO bands (10.7 volts), comet-tail bands (16.7 volts), first negative carbon bands and the "combination bands" of CO^+ (19.8 volts).

53. The structure of molecules. Raymond T. Birge, University of California.—Recent developments in band spectra indicate that there are in diatomic molecules electronic energy levels which may be designated s, p, etc., and which have a multiplicity similar to that of a certain "corresponding" atom. New quantitative examples of this are given for CO, N_2 and NO. The results for CO (previous abstract), together with those for N_2, H_2 and He_2, indicate that these molecular levels are given also at least approximately by the *formulas of line spectra.* Hence the structure of the outer electrons of molecules must be very similar to that of the "corresponding" atom (CO and N_2 like Mg, CO^+ and N_2^+ like Mg^+, CN and BO like Na, NO like Al, etc.), as already suggested by Mulliken and Mecke. Moreover, in CO, CO^+, NO, CN and BO, the frequency of vibration of the dipole is less, and consequently the moment of inertia is greater, when the radiating electron is in a p level, than when in any s level. This seems to be evidence that the radiating electron moves in a protruding path, to give the valence properties, which also penetrates to varying degrees the region *between the two nuclei,* and so plays a definite role in determining the strength of the chemical bond.

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THE
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THE NATURAL BETA-RAY SPECTRUM OF RaD*

BY L. F. CURTISS+

ABSTRACT

The natural β-ray spectrum of RaD has been photographed and the energies of its lines directly compared with those of the RaB β-ray spectrum in the same region. The RaB line $H\rho=660.9$ as measured by Ellis and Skinner[1] has been taken as a standard reference line. The following values for the energies of the lines have been determined:

No.	Intensity	$H\rho$	Energy (volts$\times 10^{-6}$)
1	50	594.3	0.3033
2	3	600.3	0.3092
3	25	709.1	0.4268
4	10	735.2	0.4576
5	1	742.5	0.4663

No. 5 is a line which has previously escaped detection. The analysis of this spectrum for determining the energy of the γ-ray responsible for it shows conclusively that the γ-ray is emitted *after* the disintegration. This is in accord with Meitner's[2] view. The energy of the γ-ray is determined as 0.467×10^6 volts.

INTRODUCTION

THE present interpretation of β-ray spectra has led to two views regarding the emission of the γ-ray. Ellis[3] originally contended that the γ-ray was emitted before the disintegration, i.e., before the emission of the nuclear or primary β-ray. On his view of course the secondary β-rays should have energies related to the energy levels of the atom before disintegration. Meitner,[2] on the other hand, concluded that the γ-radiation follows the disintegration and is a direct result of the disturbance of the nuclear levels occasioned by the ejection of the primary β-ray and the transition from one nuclear system to the other.

The settlement of this question is important. However, the experimental material which throws definite light on the problem is still very meager. In the majority of cases the measurements of β-ray spectra may be interpreted in terms of either hypothesis. This ambiguity arises from the nature of the β-ray spectrum. The accepted interpretation of the β-ray line spectra is that the lines represent groups of electrons which have been ejected from the x-ray levels of the atom by γ-radiation from the nucleus of the atom itself. The velocities of these electron groups are measured by bending them in a uniform magnetic field. The velocity is proportional to the product $H\rho$, where H is the intensity of the magnetic field, and ρ the radius of the circle on which the β-particles travel. For the harder β-radiation of RaB and for all lines in the RaC β-ray spectrum, the observed $H\rho$ should differ by less than one-half percent if the atomic levels for $Z=83$ were used instead of those for $Z=82$. (Since RaB is an isotope of lead and disintegrates into RaC, an isotope of bismuth, these are the two atomic systems with which we are concerned in this case.) This difference is beyond the limit of accuracy of most experiments. However, Ellis and Skinner[1] in their more precise measurements of the RaB β-ray spectrum, find that in the "*C*" region they are forced to use atomic levels for $Z=83$ instead of 82 in order to obtain agreement for the energy of the γ-ray. This is the most decisive previous evidence in favor of Meitner's hypothesis.

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* Published by permission of the Director of the Bureau of Standards, Department of Commerce.

+ National Research Council Fellow.

[1] C. D. Ellis and H. W. B. Skinner, Proc. Roy. Soc. **105,** 165 (1924).

[2] L. Meitner, Zeits. f. Physik **11,** 35, (1922).

[3] C. D. Ellis, Proc. Cam. Phil. Soc. **21,** 121 (1922).

It is clear that further evidence on this question can be obtained by studying other radioactive elements which emit comparatively soft γ-radiation. Under such circumstances the secondary electrons of the β-ray spectrum will have lower velocities and therefore energies more nearly comparable with the energies of the atomic levels. The natural β-ray spectrum of RaD is well suited to this purpose. RaD is an isotope of RaB and emits a single γ-ray of energy considerably less than that corresponding to the K limit for this atom. Consequently its β-ray spectrum contains electrons from the L level and levels of lower energy. Numerous measurements have been made of this spectrum but there is still great divergence of opinion concerning it. Various observers disagree even on the number of lines that it contains. For example, Ellis[3] observed five lines whereas Meitner[2] later found but three. For convenience previous results are tabulated below. The quantities given under the name of each author are the values of $H\rho$ for lines which they observed in the RaD β-ray spectrum.

The weight of evidence favors a β-ray spectrum of four lines, as originally reported by Danysz. The most recent measurements are by

TABLE I

$H\rho$ values of RaD β-ray spectrum by previous investigators

Danysz[4]	Ellis[3]	Meitner[2]	Black[5]
602	600	602	600
607	605	—	606
—	628	—	—
718	717	718	714
743	742	741	738

Black.[5] These differ from Danysz's by an approximately proportional decrease of the energy of all lines. The failure of certain investigators to detect some of these lines has given rise to considerable discussion regarding their physical significance.[2]

EXPERIMENTAL RESULTS

With the hope of throwing further light on the problem of the emission of the γ-ray, I have taken a number of photographs of the RaD β-ray spectrum. The spectrograph was of the usual type, but with large dispersion ($\rho_{max}=7.5$ cm). The magnet was one specially designed for the study of β-ray spectra. It has poles 24 cm in diameter and gives a field uniform to one part in 2000 by actual measurement over a circle 15 cm in diameter. This magnet and the spectrograph will be fully described elsewhere.[6] The magnet was excited by an independent set of storage batteries. The current was measured and controlled by a Leeds & Northrup potentiometer and standard resistance in the usual manner. It was found comparatively easy to maintain the current constant to at least one part in 2000 over long periods of time. In order to avoid the trouble of precise absolute measurement of the intensity of the magnetic field, comparison photographs of RaB lines in the same region were made. The line $H\rho=660.9$, as measured by Ellis and Skinner,[1] was used as a reference line and their value for its energy was accepted as a standard. The lines of the RaD spectrum here reported have thus been measured in terms of this value. It is obvious that the absolute energies of the lines observed here must be as accurate as this value, since a direct comparison of this kind can be made with great precision. Eastman x-ray plates were found at least 50 percent more sensitive than ordinary plates to β-radiation in this region. This test was made by exposing a plate of each kind simultaneously in the spectrograph and developing the two plates together. Consequently all exposures were made with x-ray plates. The RaD sources were obtained by the anodic deposition on a fine platinum wire in the usual way. Two different preparations of RaD were used, both giving identical results.

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[4] Danysz, Le Radium **10,** 4 (1913).

[5] Black, Proc. Roy. Soc. **109,** 166 (1925).

[6] L. F. Curtiss, J.O.S.A. and R.S.I. in press.

The experiments were carried out as follows: The current through the magnet was adjusted to the desired value and after several reversals the switch was thrown to the "direct" position. A source of RaD was inserted into the spectrograph by means of a ground glass joint, the photographic plate having been previously put in position. The spectrograph was then exhausted by a large diffusion pump. A shutter, manipulated by a ground glass joint, protected the plate from β-radiation during the period of exhaustion, which usually was of the order of 20 minutes. After a sufficient exposure the shutter was closed, air admitted, the spectrograph opened, and the plate removed. A fresh plate was then inserted. The RaD source was replaced by a source consisting of the active deposit of radon and a new exposure made. Throughout this time the current through the magnet was maintained constant at its original value with a high degree of accuracy. Thus the second exposure gave the β-ray spectrum of RaB in the same magnetic field. A fiducial mark put on the plate while still in the spectrograph permitted the determination of its position relative to the apparatus. Several experiments were performed in this manner. The measurements on all plates agreed with each other to at least one part in 1000. The results are tabulated below.

TABLE II

$H\rho$ and energy values of RaD β-ray spectrum

No.	$H\rho$	Intensity	Energy (volts $\times 10^{-6}$)
1	594.3	50	0.3033
2	600.3	3	0.3092
3	709.1	25	0.4268
4	735.2	10	0.4576
5	742.5	1	0.4663

The first four lines given above are those originally reported by Danysz in 1913, but the $H\rho$ values and the energies are considerably lower. In addition a faint line of higher energy has been observed which has previously escaped detection. This line appeared on all plates and there is no doubt of its existence, although it is too faint to measure with the same accuracy as the other lines. The value here given was determined from measurements of the plates independently by Mr. R. L. Chenault and by myself. As can be seen from the photographic reproductions, Plate I, there is no trace of the line $H\rho = 628$ reported by Ellis. A careful scrutiny of all plates failed to reveal it. The line $H\rho = 600.3$ (No. 2 in Table II) is clearly visible even in the photographic reproduction although Meitner failed to detect it. This failure was presumably due to the low dispersion with which she worked. The photographs reproduced in this paper are about one and a half times actual size, and illustrate the dispersion employed. *A* is a reproduction of one of the spectrograms for RaD and *B* shows the comparison spectrum of RaB.

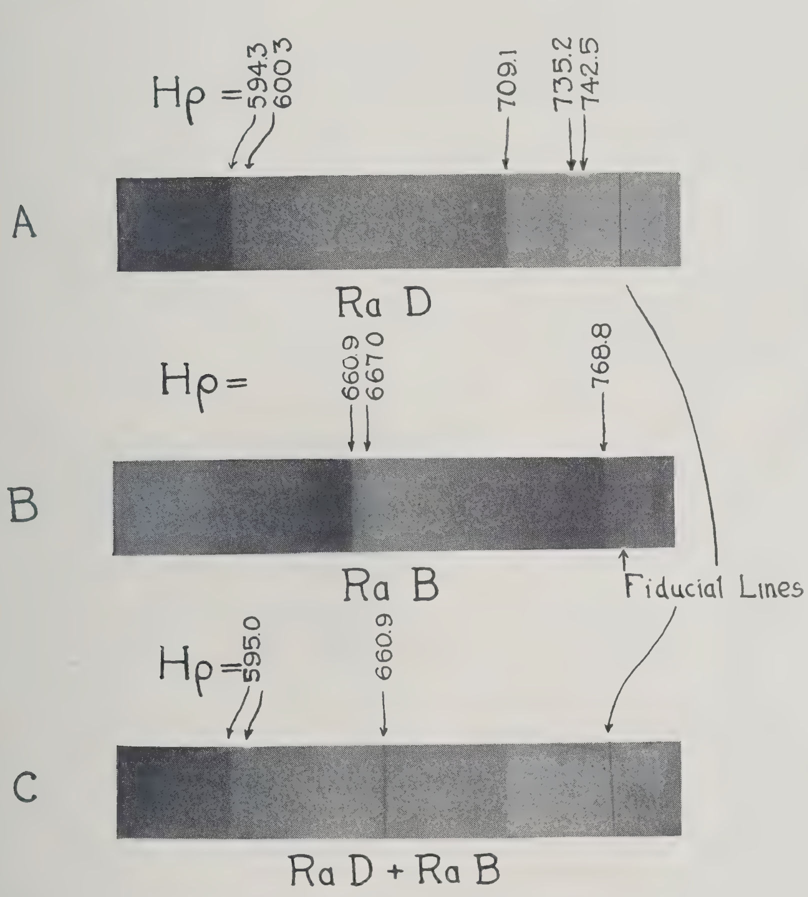

Plate I. Beta-ray spectra of RaD and RaB.

Since the values given in Table II differ consistently by at least one percent from the best previous measurements, a control experiment was considered necessary. The only objectionable feature of the foregoing procedure is the necessity for removing both plate and source between the RaD exposure and the calibration exposure with RaB. It would be much better to obtain the calibration simultaneously with the RaD exposure. Obviously only one line in the one spectrum need be checked against a corresponding line in the other. To this end the fine platinum wire on which the RaD had been deposited was exposed in radon in the usual way and activated with RaB. The wire was then placed in the spectrograph and the two spectra obtained on one plate by the single exposure. The measurements of this plate follow:

	ρ(observed)	$H\rho$	
RaB	6.365 cm	660.9	(Ellis and Skinner)
RaD	5.733 cm	595.0	(calculated)

These lines selected for comparison are the strongest lines in this region of each spectrum. As the above table indicates, the calculated value of $H\rho$ for the RaD lines is 595.0, in good agreement with 594.3 obtained from the first series of experiments. This combination photograph is reproduced in Plate IC.

The importance of the new line $H\rho=742$ becomes evident when we consider the energy of the γ-ray responsible for this β-ray spectrum. Table III gives the energies corresponding to the observed $H\rho$ values. These energies, increased by the energy of the appropriate x-ray level as indicated, are computed for $Z=82$ and 83.

TABLE III

Energy of γ-ray from RaD

		$Z=82$		$Z=83$	
$H\rho$	Energy (volts $\times 10^5$)	Level of origin	Energy of γ-ray (volts $\times 10^{-5}$)	Level of origin	Energy of γ-ray (volts $\times 10^{-5}$)
594.3	0.3033	L_{I}	0.4617	L_{I}	0.4669
600.3	0.3092	L_{II}	0.4612	L_{II}	0.4663
709.1	0.4268	M_{II}	0.4623	M_{I}	0.4668
735.2	0.4576	N_{III}	0.4643	N_{I}	0.4672
742.5	0.4663	——	0.4663	——	0.4663

The levels for atomic number 82 have been selected to give the best possible agreement, leaving all other considerations aside. Even so, the agreement is very poor. To secure approximate constancy for the energy of the γ-ray, it has been necessary to omit the M_{I} level and retain the M_{II} level. In the N group only the N_{III} level can be used. Such procedure is contrary to the weight of evidence of all observers in this field. It is now a well established fact that under the conditions here considered the levels will be present in the β-ray spectrum with intensities in the order of their binding energy. If we adhere to this principle, there is no agreement whatever. The newly observed line has an energy of 0.4663 times 10^5 volts. However, the best estimate of the energy of the γ-ray as deduced from the levels of $Z=82$ in the above table is 0.462 times 10^5 volts. This involves the obvious paradox of a γ-ray causing the emission of β-radiation of still greater energy. It should be noted that the energy of the new β-ray line is more than one percent higher than that deduced for the γ-ray. This difference cannot be attributed to experimental error.

The last column of the table shows the excellent agreement obtained for the energy of the γ-ray when the levels for $Z=83$ are used. The energy is constant to one part in 500. Furthermore the intensities from the various levels follow in the order to be anticipated. Now the M_{I} level and the N_{I} level fit perfectly. No level is assigned to the new line since it is already approximately equal to the energy deduced for the γ-ray. The simplest explanation of this apparent equality is that this line represents particles ejected from the outer levels of the atom where the binding energy is relatively insignificant. The intensity favors this explanation very strongly. The other alternative is to accept Meitner's hypothesis that some at least of the primary β-radiation from the nucleus should escape with energy exactly equal to that of the γ-ray. However, the reason for such an assumption is not altogether clear. Furthermore, the intensity of this line does not agree with such an interpretation. This is discussed below.

The excellent agreement obtained for the various levels for atomic number 83 is in itself a strong argument for assuming that the γ-ray ejected the electrons in the β-ray spectrum from the levels of this atom. This means that the γ-ray is emitted after the emission of the primary β-particle when the electrons have adjusted themselves to their new energies. The fact that no agreement whatever can be obtained with the line $H\rho=742$ on the basis of the levels of atomic number 82 reinforces this argument most decidedly. Consequently it is safe to conclude that the γ-ray is emitted after disintegration in accord with Meitner's view.

The interesting question arises as to what becomes of the primary β-radiation. Ellis in his interpretation accounted for this radiation in the continuous spectrum. But he supposed the primary radiation to come after the emission of the γ-ray. Under these circumstances it is conceivable that the primary particles might come out of the nucleus with energies varying over a considerable range and thus constitute a continuous spectrum. Since it now appears fairly certain that the disintegration takes place *first*, we expect the primary particles to be emitted with sharply quantised energy. They should then of course appear as a line in the β-ray spectrum. In the case of RaD, conditions are particularly simple. It emits only one γ-ray. Therefore we should anticipate that the number of primary β-particles would be equal to the number of γ-rays emitted. If this were true the primary line would be the strongest line, since the energy of the γ-ray has been shared among the various atomic levels. This argument would rule out the line $H\rho = 742$ as a primary β-ray line.

There are at least two ways to account for the absence of the primary β-ray line. One possibility is a suggestion due to Rosseland.[7] He proposed the explanation that the particles originally leave the nucleus with a definite energy. In passing through the strong fields in the neighborhood of the nucleus they might be expected to radiate energy. He calculated this possible loss of energy by radiation and found that it was of the right order of magnitude to distribute the particles into a continuous spectrum. This explanation requires that variable portions of the energy be radiated and it is hard to see why this should happen. Much more information is needed concerning the intensity of the continuous spectrum before this question can be answered. Another possibility, though a somewhat doubtful one, enables us to eliminate both the continuous spectrum and the primary line from the β-ray spectrum. If we adopt Meitner's view and assume that the primary particle has energy exactly equal to that of the γ-ray, we may suppose that this primary particle experiences an inelastic collision with the first electron in the atomic levels which has less binding energy than that of the primary particle. The result would be a binding of the β-particle in the atomic level and the ejection of the electron originally in the level. However, this ejected electron should have exactly the same energy as those expelled by the γ-radiation. Therefore they would form part of the same line on the photographic plate. Presumably this could take place at other levels of lower energy so that most or all of the primary particles were absorbed. Therefore we should have little or no primary β-radiation and no continuous spectrum. The great difficulty with this hypothesis is that such collisions from any ordinary point of view must be relatively improbable. However, to explain the intensity of the lines, considering all γ-radiation to be converted in the atomic levels of the atom from which it originates, we are forced to assume an abnormally high coefficient of absorption for the γ-ray. It may well be that the same is true for a β-particle travelling from the nucleus out through the various electron levels. Since there is considerable radiation from neighboring atoms present, some support for this view can also be obtained from Milne's[8] statistical analysis of the liberation of photo-electrons. He finds that he is compelled to assume that external radiation can stimulate the capture of an electron. This might make it possible to account for the high probability of capture necessary on this view.

In conclusion, I should like to thank Dr. S. C. Lind of the Fixed Nitrogen Laboratory, for providing me with the old radon tubes from

[7] Rosseland, Zeits. f. Physik **14,** 173 (1923).

which the RaD sources were obtained, and Dr. Bardwell for much valuable advice concerning the manipulation of this material.

Note added to proof: Since the above paper was submitted for publication the library has received the issue of the Proceedings of the Cambridge Philosophical Society for November, 1925. A series of remarkable papers in this number present evidence indicating that the gamma-ray follows the disintegration for RaB and RaC. Rutherford and Wooster (Proc. Camb. Phil. Soc. **22**, 832, 1925) show that RaB emits the natural L spectrum of atomic number 83. Of course this is not a conclusive proof of the emission of the gamma-ray after disintegration. There is a possibility that the gamma-ray is emitted before disintegration but that the *x-ray transitions* are delayed and occur after the disintegration. The significant point of their result is that it does not contradict the supposition that the disintegration occurs first. If, on the other hand, the x-ray spectrum of atomic number 82 had been obtained there could be no doubt that the disintegration followed the gamma-ray emission. In confirmation of the results obtained by Rutherford and Wooster, Black has measured some of the lines of the natural L beta-ray spectrum of RaB. He also finds that these correspond to atomic number 83. Since this phenomenon is one step further removed from the emission of the gamma-ray than the one investigated by Rutherford and Wooster, it likewise does not constitute a *proof* that the gamma-ray follows disintegration. However, Ellis and Wooster (Proc. Camb. Phil. Soc. **22**, 844, 1925) have devised an experiment which seems to give definite proof. They wrapped a radon tube in platinum foil and then exposed the platinum surface in radon and obtained the active deposit on the outside of the platinum wrapping. Using this as a source in a beta-ray spectrograph they obtain the natural beta-ray spectra of RaB and RaC from the active deposit and the similar spectra excited in the platinum foil by the gamma radiation from the radon. They thus obtain a $\delta H\rho$ for each of the observed lines corresponding to the difference between the K, L, etc., energy for platinum and for RaB and RaC. This enables them to determine whether these levels are those of 82, 83 or 84. The measurements given in their paper very decidedly favor atomic number 83 for the lines of the RaB spectrum and atomic number 84 for the lines of the RaC spectrum. These results are thus a confirmation of the hypothesis proposed by Meitner that the disintegration *precedes* the emission of the gamma-ray, and there now seem to be no exceptions to this rule.

Bureau of Standards,
Washington, D. C.,
December 15, 1925.

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[8] E. A. Milne, Phil. Mag. **47**, 222 (1924).

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THE ABSORPTION OF X-RAYS OF WAVE-LENGTH DOWN TO .08A

By S. J. M. Allen

Abstract

Mass absorption coffiecients of C, paraffine, S and 16 metal elements from Al to U for wave-lengths .56 to .08A have been measured in continuation of previous work[1] which covered most of these elements in the range .71 to .10A. The general radiation from a tungsten target (operated at voltages up to 200 kv) was dispersed by a crystal into an ionization chamber. By using Soller multiple slit collimators about ten times as great intensity was obtained as with a single slit of the same resolving power. The main results of the previous paper were confirmed and extended, especially the steady decrease in the "jump" of the absorption in going from the L to the K regions, as the atomic number increases. The scattering of paraffine wax is distinctly greater than that of C or Al, probably due to the richness of H in paraffine. The empirical formula $\mu/\rho = C\lambda^{2.92}N^4/A + \sigma/\rho$, applied to the experimental results gives values of σ/ρ which increase in general with atomic number, becoming about 1 for the heavier elements, W to Bi. The values of C obtained are .0132 for the K series and .00181 for the L series; these give calculated values which agree within 5 percent with the experimental. *Experiments with end-filtered high voltage rays.* Without collimators or crystal, the ionization chamber in the path of the direct beam of rays filtered through 1 cm tin and 2 cm aluminum, showed increased ionization when a carbon block was interposed, but when two Soller collimators were used with planes crossed so as to eliminate all oblique rays, normal absorption coefficients were obtained corresponding to .075A. This method may be useful for the shortest rays.

IN a previous paper[1] the author gave results of experiments on the absorption of homogeneous x-rays from $\lambda = .71$ to .10A following the standard method of reflecting the general radiation of a Coolidge tube from a crystal, and intercepting a narrow portion of the spectrum with an ionization chamber attached to the spectrometer.

It was shown that as the wave-length approached .10A, the K absorption coefficients of the high weight elements were decreasing steadily according to the laws of fluorescent absorption, but that in the case of the light elements fluorescent absorption being practically gone, further decrease was very slow. Also, that in the critical absorption regions of the elements the "jump" of the absorption coefficients from the L series to the K series became steadily less with increasing atomic number. This was especially marked in the case of the elements from W to Bi, with the result that the K absorption coefficients of these elements were nearly the same.

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[1] Allen, Phys. Rev. **24,** 1 (July 1924).

It was further shown that the Bragg-Owens' empirical absorption law, $\mu/\rho = C\lambda^3N^4/A + \sigma/\mu$ was no longer able to predict values of μ/ρ for the high weight elements which agreed with the experimental values obtained. In all the discussion which follows in this paper μ/ρ will represent the experimentally determined mass absorption coefficient, τ/ρ the fluorescent absorption coefficient of the electronic orbits, (K, L, M, etc.), and σ/ρ the remainder of the absorbed energy, which may or may not be entirely due to pure scattering.

The present paper is a continuation of the above work, and carries the wave-length down to .08A. While these experiments were carried out in the same general manner as the former ones, the technique of operation was so different as to necessitate a brief description.

The source of the rays, up to a potential of 120 kv was a Coolidge Universal tube,and up to 200 kv a Coolidge high tension tube. The tube, generator, and all high tension connections were placed by themselves in a closed room, completely shut off from the adjacent room, where the spectrometer was placed, by a brick wall two feet thick and lined with lead. A hole was pierced through the wall and two lead slits 1 cm square placed at each end, defined the beam of rays from the tube.

In place of the usual single slit method, the multiple slit collimators, devised in my laboratory by Soller[1] were employed. The first collimator was placed directly in front of the crystal with its axis passing through the axis of rotation of the spectrometer and perpendicular to it. The second collimator was attached to the ionization chamber, and in the zero position its axis was coincident with that of the first. Each collimator was 8 cms long, 1 cm wide, 1 cm high and had slits about .2 mm wide.

The general radiation passing through the first collimator emerged as a number of thin beams parallel to each other in a vertical plane. This beam falling upon a calcite crystal 2 cms thick passed through it, the reflected radiation being obtained from the interior 100 planes. The zero position having been determined, the ionization chamber was swung around to some angle 2θ. The crystal was now rocked back and forth until maximum radiation was received, when it was assumed that radiation of wave-lengths between λ and $\lambda + d\lambda$ alone passed through the second collimator. The mean wave-length λ was calculated from the relation, $\lambda = 2d \sin \theta$.

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[1] Soller, Phys. Rev. **24**, 158 (1924).

The resolving power was quite equal to that obtained with single slits of .1 to .2 mm.

It was found that this method gave about ten times the intensity that could be obtained with single slits at the same resolving power. Another great advantage of this method lies in the fact that the zero position once having been obtained does not change with penetration of the rays into the crystal, δ being obtained solely from 2θ the angle between the axes of the two collimators.

The rest of the experiment was carried out in the usual manner, the absorbing layers being placed on the side of the wall next to the tube, thus ensuring that no scattered radiation from these layers could enter the ionization chamber.

Although rays reflected from the crystal at values of θ less than that corresponding to $\lambda = .081$A were observed, difficulties of resolution were encountered which rendered them somewhat uncertain, and so results are here given only down to $\lambda = .081$A. It is hoped that a redesign of

TABLE IA

Mass absorption coefficients μ/ρ

λ in A	C	Paraffine	Al	S	Fe	Ni	Cu	Zn	Pd
.081	.143	.156	.145	.155	.235	.265	.270	.310	.73
.085	.145	.158	.153	.170	.242	—	.280	—	.80
.090	.148	.160	.160	.182	.250	.290	.295	.350	.86
.095	.150	.165	.164	.186	.262	—	.305	—	—
.102	.150	.171	.169	.192	.280	.337	.335	.390	1.11
.113	—	—	—	—	.317	—	.405	—	—
.118	.151	.175	.172	.196	.360	—	.440	.520	—
.126	—	—	—	—	.410	.480	.510	—	—
.135	—	—	—	—	.460	—	.600	.690	—
.140	.152	.180	.195	.250	.500	—	.650	—	—
.145	—	—	—	—	.540	—	.710	.820	—
.148	—	—	—	—	—	—	—	—	—
.151	.153	—	—	—	.595	.690	.780	—	—
.160	—	.185	.212	.295	.660	—	.900	1.02	—
.164	—	—	—	—	—	—	—	—	—
.173	.155	.190	.235	.330	.780	1.00	1.09	1.24	—
.185	—	—	.249	.360	.90	1.18	1.30	1.47	—
.194	—	—	.265	—	1.00	—	—	—	—
.209	.166	.196	.295	.440	1.26	1.63	1.71	2.01	—
.220	—	—	.310	.500	1.40	—	2.00	2.32	—
.240	.170	.200	.356	.580	1.75	2.28	2.50	2.80	—
*.280	—	—	.475	.800	2.75	3.38	3.70	4.30	—
*.320	.200	.220	.630	1.08	3.95	4.87	5.25	6.20	—
*.340	—	—	.730	1.23	4.65	5.75	6.38	7.30	—
*.400	.245	.245	1.11	1.78	7.25	—	8.80	11.6	—
.430	—	—	1.33	2.10	—	—	12.5	14.5	—
.458	.288	—	1.54	—	—	—	14.7	17.2	—
.511	—	.34	2.06	—	—	—	20.5	24.0	—
.560	.40	.36	2.65	—	—	—	26.5	30.8	—
*.631	.55	—	3.78	6.9	—	—	37.8	43.0	—
*.710	.68	—	5.35	9.9	—	—	53.7	60.0	—

* Taken from previous paper.

the apparatus will in the future enable me to obtain results for shorter wave-lengths.

In Tables IA and IB are tabulated results of this work, and also a number of the results of the preceding work, which are indicated by asterisks. The vertical double arrows indicate the regions of critical absorption, the upper limit being the highest K values, and the lower the lowest L values. In the cases of Ba, Th, and U, the values given are the values which probably would have been obtained if these substances had been in the pure state. They were calculated assuming the additive law. Păraffine was in the form of paraffine wax.

TABLE IB

Mass absorption coefficients μ/ρ

λ in A	Ag	Sn	Ba	W	Pt	Au	Pb	Bi	Th	U
.081	.74	.80	—	2.40	2.50	2.44	2.53	2.50	—	—
.085	.83	.88	—	2.60	2.75	2.65	2.78	2.76	—	—
.090	.90	.95	—	2.80	2.95	2.85	3.00	3.00	—	—
.095	1.02	1.02	—	3.10	3.38	3.30	3.45	3.45	—	3.53
.102	1.17	1.20	—	3.50	3.80	3.76	3.90	3.90	4.00	↕
.113	—	1.52	—	4.30	4.50	4.48	4.70	4.70	↑	1.78
.118	1.57	1.77	1.95	4.75	5.00	4.90	5.13	4.90	↓	—
.126	1.68	2.05	—	5.35	5.70	5.50	5.23	↑	1.86	1.90
.135	—	2.40	—	6.25	6.55	6.40	↑		2.10	—
.140	2.40	2.62	2.80	6.75	7.08	6.90		↓	2.25	2.56
.145	—	2.90	—	7.30	7.55	7.40		2.25	2.48	—
.148	—	—	—	7.75	7.70	↑	↓	—	—	—
.151	2.65	3.15	3.40	8.00	↑		2.45	2.48	2.72	3.78
.160	—	3.60	4.00	8.90		↓	2.70	2.90	3.10	—
.164	—	—	—	↑	↓	2.70	—	—	—	3.24
.173	3.75	4.32	4.90		2.90	3.02	3.25	3.50	3.75	—
.185	4.40	5.05	5.80	↓	3.48	3.55	3.85	4.14	4.45	—
.194	5.00	—	7.0	3.20	3.90	—	4.40	—	5.05	—
.209	6.50	6.95	8.2	3.93	4.70	4.87	5.35	5.60	6.10	—
.220	7.40	8.30	9.2	4.20	5.25	5.50	5.90	6.48	6.90	—
.240	9.60	10.80	11.7	5.10	6.65	6.95	7.40	8.30	8.60	—
*.280	14.8	15.5	17.2	7.20	9.60	—	11.5	12.5	—	—
*.320	21.1	22.0	24.2	10.1	13.5	—	16.2	17.7	—	—
*.340	24.5	—	6.0	12.0	15.8	—	19.7	21.0	—	—
*.400	38.2	—	9.0	19.8	24.5	—	31.8	—	—	—
		↕								
.430	46.5	8.0	11.5	24.7	30.0	—	39.0	—	—	—
.458	60.0	9.0	13.7	29.7	35.5	—	46.0	—	—	—
	↕									
.511	10.0	12.8	19.0	—	—	—	—	—	—	—
.560	15.0	16.5	—	—	—	—	—	—	—	—
*.631	20.5	—	—	75	87	—	101—	—	—	—
*.710	28.5	—	—	—	119	—	140	—	—	—

* Taken from previous paper.

Table II gives the values of the critical absorption wave-lengths as obtained from the data of Tables IA and IB. These values agree in general to within one percent with those published by other observers.

A detailed study of the absorption coefficients of Tables IA and IB shows that they are of the same character as those of the preceding work. The "jumps" in the values of τ/ρ from L series to K series steadily decrease with increasing atomic number, that for U being about 4. The K absorption coefficients from W to U are nearly all the same, for the same wave-lengths, and it would require an accuracy of one percent or better to decide whether there is any real difference. The decrease in μ/ρ with λ is about the same for all. The intermediate elements, such as Ag, Sn and Ba, show values of σ/ρ which decrease much more slowly with λ, indicating that σ/ρ which decreases slowly is becoming of increasing importance in comparison with τ/ρ. The values of μ/ρ for the light elements as $\lambda=.08$A is approached show such small rates of change, that for these elements τ/ρ is fast disappearing as an important factor, and σ/ρ is now the predominating factor. In the case of C the change in μ/ρ from $\lambda=.160$ to $\lambda=.081$A is only a few percent, and even this small rate of decrease is becoming smaller as we approach .08A. The same is true of paraffine, Al and S. μ/ρ for paraffine wax at $\lambda=.081$A is distinctly greater than that of C or Al, whilst at $\lambda=.40$A it is equal to that of C and much less than that of Al. This can be probably explained by assuming that σ/ρ for H is greater than that for C, for since paraffine wax is rich in H, it will show correspondingly larger values of σ/ρ and smaller values of τ/ρ than C.

TABLE II

Critical absorption wave-lengths λ_c

Element:	U	Th	Bi	Pb	Au	Pt	W	Ba	Ag
λ_c in A:	.105	.113	.132	.139	.154	.159	.178	.330	.484

The same phenomenon has been found for substances rich in H by other observers at longer wave-lengths.

There is no evidence that σ/ρ is experiencing any sudden or rapid decrease with λ.

If we are justified in concluding from the above results that the true mass scattering coefficient for light elements will continue to decrease at such a slow rate it is difficult to see how it can arrive for $\lambda=.02$A at such a low value for C as .056 for the filtered γ rays of radium C, which the recent work of Ahmad,[2] Ahmad and Stoner,[3] and that of Owen, Fleming and Fage[4] would seem to indicate. It is possible that there estimations of λ are much too high.

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[2] Ahmad, Proc. Roy. Soc. **A105,** 507 (1924).

[3] Ahmad and Stoner, Proc. Roy. Soc. **A106,** 8 (1924).

[4] Owen, Fleming and Fage, Phys. Soc. Proc. **36,** 355 (August, 1924).

In Table III are expressed some estimated values of, σ/ρ, calculated from the data of Tables IA and IB by aid of the formula, $\sigma/\rho=\mu/\rho-k\lambda^{2.92}$. If this formula holds for these short wave-lengths for both the K series (excluding elements W to U) and the L series, the results indicate that σ/ρ increases with N, reaching in the L series of the heavy elements values possibly as high as 1.0. Similar results are obtained if we use λ^3, only they are larger.

TABLE III

Mass scattering coefficients, $\sigma/\rho=\mu/\rho-k\lambda^{2.92}$

Element	λ.08A	λ.120A	λ.210A	λ.320A	λ.440A
		K series			
Carbon	.142	.148	.151	.148	.145
Paraffine	.155	.155	.184	.180	.169
Aluminum	.136	.144	.150	.130	.140
Sulfur	.138	.144	.170	.150	—
Iron	.165	.160	.200	.21	.25
Copper	.175	.160	.24	.03	—
Zinc	.195	—	—	—	—
Silver	.370	.43	.50	.3	—
Tin	.380	.45	—	—	—
Barium	—	.51.	.70	—	—
		L series			
Tungsten	.9 to 1.0	.75	1.0	—	—
Platinum					
Gold		1.0	1.2		
Lead		1.1	1.1		
Bismuth		.9	1.0		

Now, if σ/ρ, which here merely means the rest of the energy lost after fluorescent absorption has been allowed for, is completely due to pure scattering, then it should decrease in general with increase of N, being proportional to N/A in any of the theoretical formulas of, Thomson, Compton, or Jauncey.

It is evident that either one cannot use these empirical formulas to predict the values of τ/ρ at these short wave-lengths, or, if one can, then the values of σ/ρ so obtained are much larger in many cases than the theoretical formulas of pure scattering would indicate.

It is also possible that the experimental values of σ/ρ are not wholly due to pure scattering, but may involve some form of absorption, either true absorption, or scattering, or both, not associated with the K, L, etc. orbits, such as perhaps nuclear absorption.

It is important to call attention to the fact that Barkla and his associates in several papers on relative scattering state that the relative scattering of heavy elements to light elements increases rapidly with N, and also with λ.

Also Debye[5] from theoretical considerations predicts, that in the case of scattering from atoms where the electrons are not free but concentrated near the center, the atomic scattering coefficient would be proportional to a higher power of N than the first, in the limiting case (electrons at the center) being proportional to N^2. For mass scattering this would give σ/ρ proportional to $N^2/2$ instead of N/A.

Until one has obtained by a direct method true values of σ/ρ, it may not seem very fruitful to try to distinguish, in the region of short wave-lengths, between the various empirical absorption formulas. The generally accepted one is

$$\left.\begin{aligned}\mu/\rho&=C\lambda^3N^4/A+\sigma/\rho\ldots\ldots\ldots\ldots\ldots\ldots(\text{mass})\\ \mu_a&=C_a\lambda^3N^4+\sigma_a\ldots\ldots\ldots\ldots\ldots\ldots(\text{atomic})\end{aligned}\right\}(1).$$

The author has proposed the following—

$$\left.\begin{aligned}\mu/\rho&=C\lambda^{2.92}N^4/A+\sigma/\rho\ldots\ldots\ldots\ldots\ldots(\text{mass})\\ \mu_a&=C_a\lambda^{2.92}N^4+\sigma_a\ldots\ldots\ldots\ldots\ldots(\text{atomic})\end{aligned}\right\}(2)$$

Within the limits in which these formulas may be used to predict results to about five percent, I have, from the data of these two papers, and from those given by Bragg and Pierce,[6] Hewlett,[7] Richtmyer,[8] Windgarth,[9] and Stoner and Martin,[10] calculated the best values of C and C_a. These are expressed in Table IV.

TABLE IV

Values of C and C_a

	K series		L series	
	Eqs. (1)	Eqs. (2)	Eqs. (1)	Eqs. (2)
C	1.36×10^{-2}	1.32×10^{-2}	1.86×10^{-3}	1.81×10^{-3}
C_a	2.24×10^{-26}	2.19×10^{-26}	3.06×10^{-27}	3.00×10^{-27}

The experimental data of Tables 1A and IB discussed above are also illustrated by the graphs of Figs. 1, 2, 3, and 4. Figs. 1 and 2 show the relations between μ/ρ and $\lambda^{2.92}$. Figs. 3 and 4 show the relations between μ/ρ and N^4/A. Values of J from the graphs of 1 and 2 are tabulated. Also values of C_K and C_L are tabulated from Figs. 3 and 4.

In order to ascertain what reliance could be placed upon "end" filtered rays at high voltage, the following experiments were made at 200 kv.

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[5] Debye, Ann. d. Physik **46,** 809 (1915).

[6] Bragg and Pierce, Phil. Mag. **8,** 608 (1914).

[7] Hewlett, Phys. Rev. **17,** 284 (1921).

[8] Richtmyer, Phys. Rev. **18,** 13 (1921).

[9] Windgarth, Car Bloms Boktrycheri, Lund (1923).

[10] Stoner and Martin, Proc. Roy. Soc. **A107,** 1925.

The two collimators being removed temporarily, and the ionization chamber turned to the zero position, a filter of 1 cm tin and 2 cms aluminum was placed next to the tube. A reading of the electroscope was then taken in arbitrary units, say 100. A block of carbon was then

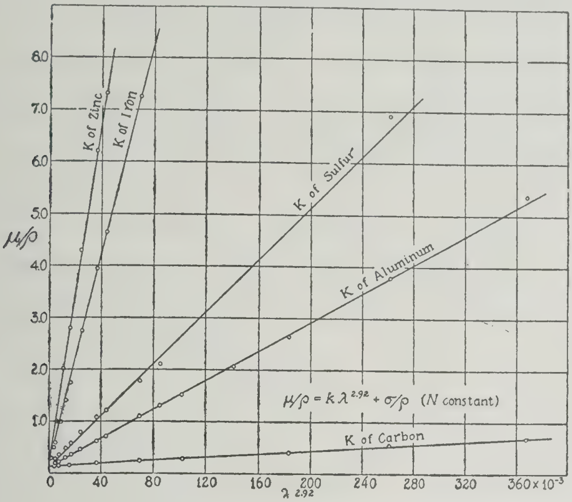


Fig. 1. Variation of μ/ρ with $\lambda^{2.92}$.

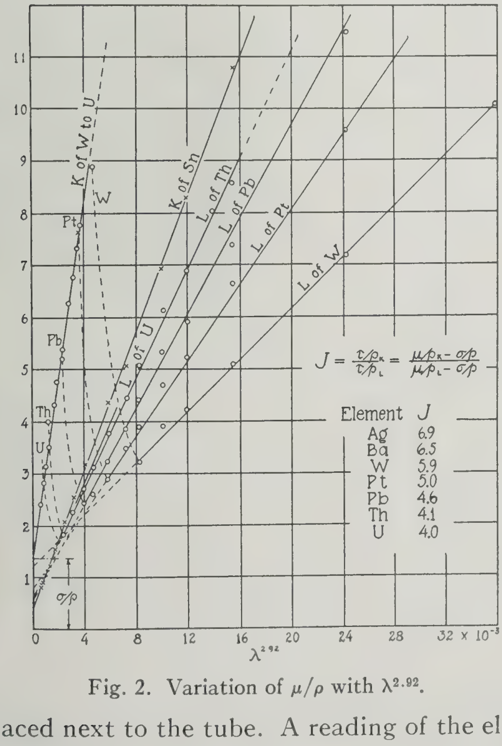


Fig. 2. Variation of μ/ρ with $\lambda^{2.92}$.

placed directly behind the filter to intercept the rays before they passed through the wall. The somewhat surprising result was now obtained that the ionization was increased to 300 instead of being decreased.

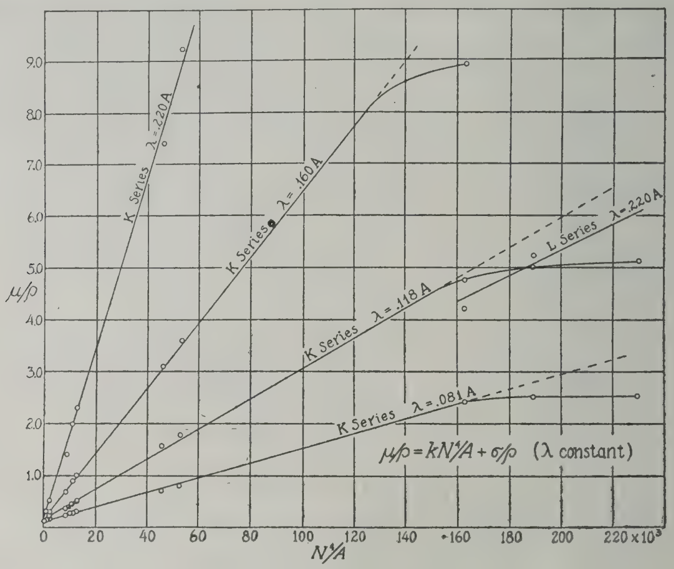
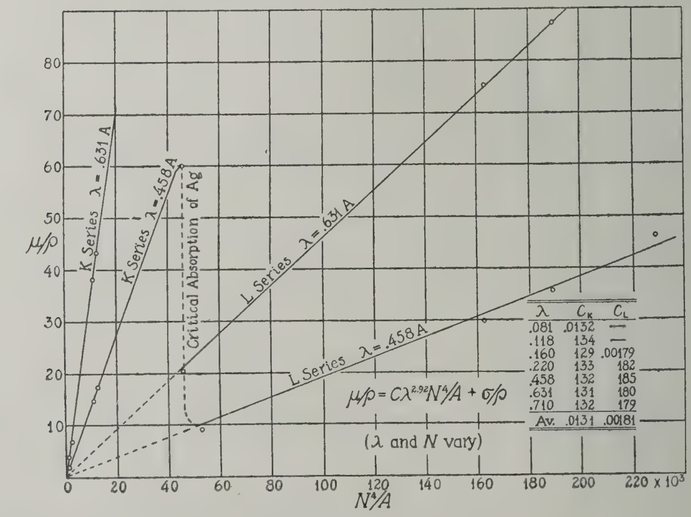


Fig. 3. Variation of μ/ρ with N^4/A.



λ	C_K	C_L
.081	.0132	—
.118	134	—
.160	129	.00179
.220	133	182
.458	132	185
.631	131	180
.710	132	179
Av.	.0131	.00181

Fig. 4. Variation of μ/ρ with N^4/A.

The same result was obtained with other elements, but in a lesser degree for the heavier elements. It is thus seen that more rays were scattered in the direction of the direct beam, than were scattered away. Under these conditions absorption coefficients would have no true significance.

Next the collimators were placed in position, with axes coincident but with their planes crossed at right angles. Readings taken now, show normal results, and it makes no difference where the absorbing layer is placed. Only those rays which pass straight forward can enter the ionization chambers, all oblique rays in both horizontal and vertical directions being eliminated.

In Table V are given the results of this last experiment. The effective wave-length viz. $\lambda = .075$A was calculated from μ/ρ for Ag and Sn. The values in this table are in good conformity with those obtained by the crystal method at $\lambda = .08$A.

TABLE V

X-rays filtered through Sn, voltage 200,000, $\lambda_{\text{eff.}} = .075$ A

Element:	C	Par.	Al	S	Fe	Ni	Cu	Zn	Ag	Sn	Pt	Au	Pb	Bi
μ/ρ	.140	.145	.147	.155	.22	.24	.25	.28	.69	.72	2.02	2.12	2.33	2.42

Since at these high voltages the energy of the spectrum is largely concentrated in the short wave-lengths, "end" filtering with crossed collimators will give results of some importance, when one is no longer able to obtain homogeneous rays from crystal reflection, at least in those elements which are far removed from their critical absorption regions.

Absorption coefficients obtained in the past from filtered "end" rays which have seemed to indicate very small values of μ/ρ at high voltages are of doubtful value, unless precautions similar in effect to those discussed above were taken.

In conclusion it may be of advantage briefly to review the chief points brought out by the experimental results of these two papers.

A careful analysis of the absorption coefficients of the elements from C to U for values of λ between .71 and .08A, shows quite clearly that no general formula of absorption of the Bragg-Owens type can predict values which agree with experimental ones in both the L and K series by simply changing the constant. In the L series it will predict values increasingly too low, and in the K series increasingly too high, as we proceed to the high atomic weight elements. The experimental fact, that the decreasing jumps in the absorption coefficients from the L series to the K series, which results in the coefficients of the elements from W to U being nearly the same for the same wave-lengths, will explain the failure in the case of the K series.

In the case of the L series, the difference σ/ρ between the experimental value of μ/ρ and the calculated value of τ/ρ is too great to be entirely accounted for by pure scattering according to the theories of Thomson, Compton, and Jauncey. It therefore seems necessary to raise the question whether in addition to fluorescent absorption and pure scattering there may exist nuclear absorption of some kind, which in the case of high weight atoms is great enough to be experimentally distinguished.

In the case of light atoms where fluorescent absorption has practically disappeared, the experimental results show that the absorption is decreasing with λ at a very slow rate.

Until one is able to determine in a region of wave-lengths where τ/ρ is very large in comparison with σ/ρ, the exact variation of τ/ρ with λ, the method of this paper in estimating σ/ρ may be open to some question. The author is at present engaged in measuring the absorption coefficients of wave-lengths greater than 1Å and it is hoped that the results of this investigation in the near future may throw more light on the problem.

University of Cincinnati,
November 3, 1925.

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REFLECTION OF RADIATION FROM A FINITE NUMBER OF EQUALLY SPACED PARALLEL PLANES

BY T. H. GRONWALL

ABSTRACT

Equations are derived for the fractions of the incident energy which are absorbed, reflected and transmitted by $n+1$ equally spaced parallel planes, taking account of all possible internal reflections, in terms of the corresponding fractions for a single plane, a, r and t respectively. When a and r are very small, as in the case of x-rays incident on a crystal surface, they may be computed from measurements of the reflected fraction R_N for N large, and of the transmitted fraction T_n, for n small.

1. *Introduction.* In dealing with the reflection, transmission and absorption of radiation in a crystalline medium, we assume the molecules of the medium to be situated in a number of equally spaced parallel planes (and to have the familiar lattice arrangement). We assume that when a ray of intensity I strikes one of these planes, a part of it, which we denote by rI, is reflected, another part tI transmitted, and the remaining part aI absorbed, so that

$$r+t+a=1. \tag{1}$$

These constants r, t and a are assumed to be the same for all planes.

Let us consider $n+1$ of these planes, numbered $1, 2, \ldots, n, n+1$, and a ray of intensity I striking the first plane; taking into account all possible modes of reflection at one or more of the planes, a certain part T_nI will be transmitted across the $n+1$ plane, another part R_nI will be reflected, that is, will emerge on the same side of the first plane as the incident ray I, and the remaining part A_nI is absorbed by the $n+1$ planes; we evidently have

$$R_n+T_n+A_n=1. \tag{2}$$

Our problem is to express R_n and T_n (and hence, by (2), also A_n) in terms of r, t and n, and it is obviously permissible to assume $I=1$ in the following discussion.

2. *Determination of R_n and T_n for $n=0$ and $n=1$.* In the case of a single plane ($n=0$) it follows at once from the definitions that

$$R_0=r, \qquad T_0=t\ . \tag{3}$$

In the case of two planes, numbered 1 and 2, a ray of unit intensity striking plane 1 gives a reflected ray r and a ray t penetrating plane 1, and when the latter ray strikes plane 2, it gives a transmitted ray $t \cdot t = t^2$ and a ray tr reflected from plane 2 toward plane 1. At the latter plane, this tr gives a ray $t \cdot tr = t^2 r$ penetrating the plane toward the side of the incident ray, so that $t^2 r$ is a component of the total reflected ray R_1, while a ray $r \cdot tr = tr^2$ is reflected toward plane 2. This tr^2 penetrates plane 2 in the amount $t \cdot tr^2 = t^2 r^2$, which forms a component of the total transmitted ray T_1, while a ray $r \cdot tr^2 = tr^3$ is reflected toward plane 1, giving at the latter a component $t \cdot tr^3 = t^2 r^3$ of R_1 and a ray $r \cdot tr^3 = tr^4$ reflected toward plane 2, where it gives a component of T_1 equal to $t \cdot tr^4 = t^2 r^4$ and a ray $r \cdot tr^4 = tr^5$ reflected toward plane 1. Continuing in this manner, we find for the sums of the components of the transmitted and reflected rays the expressions

$$T_1 = t^2 + t^2 r^2 + t^2 r^4 + \cdots ,$$

$$R_1 = r + t^2 r + t^2 r^3 + t^2 r^5 + \cdots ,$$

or summing the geometric series to the right

$$T_1 = t^2/(1-r^2) , \qquad R_1 = r + t^2 r/(1-r^2) . \tag{4}$$

3. *The two difference equations for R_n and T_n.* Proceeding to the general case, our first step consists in setting up two difference equations (that is, recurrent formulas) connecting T_{n+1} and R_{n+1} with T_n and R_n. Consider the $n+2$ planes numbered $1, 2, \ldots, n+1, n+2$; these we divide in two layers, the first layer consisting of the planes numbered $1, 2, \ldots, n+1$, and the second of those numbered $n+1$ and $n+2$. The plane numbered $n+1$, common to both layers, is called the boundary plane between them. It will be convenient to separate the reflected ray R_n in the ray r reflected directly at plane 1 and the remainder R'_n reflected at other planes after penetrating into the layer, so that

$$R_n = r + R_n' , \qquad R_{n+1} = r + R'_{n+1} , \tag{5}$$

and (3) and (4) show that

$$R_0' = 0 , \qquad R_1' = t^2 r/(1-r^2) . \tag{6}$$

Now consider a ray of unit intensity striking the first layer at plane 1; the ray T_{n+1} transmitted through both layers is made up of components which we classify according to the number of times they cross the boundary plane between the first layer and the second. The component crossing the boundary plane once is obtained thus: let t_n' be a ray which is transmitted into the second layer after a certain number of transmissions and reflections in the planes of the first layer. Since the intensity of a transmitted ray is multiplied by t in the passage through a plane, it follows that the intensity of t_n' immediately before passing through the boundary plane is $t_n' \cdot t^{-1}$. Passing through the second layer, which consists of two planes, the intensity becomes $t_n't^{-1} \cdot T_1$, and our component is the sum of $t_n't^{-1} \cdot T_1$ extended over all partial rays t'_n; the sum of the latter being T_n, the component of T_{n+1} arising from all partial rays crossing the boundary plane once is $T_nt^{-1} \cdot T_1$. Any ray transmitted through both layers must evidently cross the boundary plane an odd number of times. Hence the next component of T_{n+1} crosses the boundary plane three times and is obtained by taking the component T_nt^{-1} arriving at the boundary plane and multiplying it by $R_1't^{-1}$, thus forming a component which has crossed the boundary plane and been reflected in the interior of the second layer, but has not yet crossed the boundary plane the second time. Observe that we multiply by $R_1't^{-1}$ and not by $R_1t^{-1}=(r+R_1')t^{-1}$, since we are not concerned with those rays that are reflected at the boundary plane without penetrating into the second layer. This component $T_nt^{-1} \cdot R_1't^{-1}$ we multiply by $R_n't^{-1}$, thus obtaining a component which has crossed the boundary plane twice and been reflected in the interior of the first layer, but has not yet crossed the boundary plane for the third time. The third crossing of the boundary plane and transmission through the second layer multiplies our component by T_1, so that the component of T_{n+1} resulting from crossing the boundary plane three times will be

$$T_nt^{-1} \cdot R_1't^{-1} \cdot R_n't^{-1} \cdot T_1 \ ,$$

where each multiplication point stands at a crossing of the boundary plane. Similarly, the component which crosses the boundary plane five times is

$$T_nt^{-1} \cdot R_1't^{-1} \cdot R_n't^{-1} \cdot R_1't^{-1} \cdot R_n't^{-1} \cdot T_1 \ ,$$

and so on. Finally T_{n+1} is the sum of all these components, so that

$$T_{n+1}=T_nt^{-1}T_1[1+R_1'R_n't^{-2}+(R_1'R_n't^{-2})^2+ \cdot \cdot \cdot] \ ,$$

or by (4) and (6)

$$T_{n+1}=\frac{tT_n}{1-r^2}\left[1+\frac{rR_n'}{1-r^2}+\left(\frac{rR_n'}{1-r^2}\right)^2+ \cdot \cdot \cdot\right].$$

The geometric series to the right converges, since $R_n<1$ by (2), so that $R_n'<1-r$ by (5) and $rR_n'/(1-r^2) \ <r/(1+r)<1$; summing the series, we obtain

$$T_{n+1}=\frac{t}{1-r^2}\cdot\frac{T_n}{1-\dfrac{r}{1-r^2}R_n'}. \tag{7}$$

Turning our attention to the reflected ray R_{n+1} and reasoning in exactly the same manner, we have first the component R_n which does not cross the boundary plane, then the component crossing the boundary plane twice which is $T_nt^{-1}\cdot R_1't^{-1}\cdot T_n$, next the component $T_nt^{-1}\cdot R_1't^{-1}\cdot R_n't^{-1}\cdot R_1't^{-1}\cdot T_n$ crossing the boundary plane four times, and so on, their sum being

$$R_{n+1}=R_n+T_n^2R_1't^{-2}[1+R_1'R_n't^{-2}+(R_1'R_n't^{-2})^2+\cdot\cdot\cdot],$$

whence, replacing R_n and R_{n+1} by $r+R_n'$ and $r+R_{n+1}'$ according to (6) and observing that the series to the right is the same as in the expression for T_{n+1},

$$R'_{n+1}=R_n'+\frac{r}{1-r^2}\cdot\frac{T_n^2}{1-\dfrac{r}{1-r^2}R_n'}. \tag{8}$$

Equations (7) and (8) are the desired difference equations.

4. *Solution of the difference equations for R_n and T_n.* We now introduce the notation

$$\rho_n=1-\frac{r}{1-r^2}R_n', \tag{9}$$

whence, by (6),

$$\rho_0=1, \qquad \rho_1=1-\frac{t^2r^2}{(1-r^2)^2}; \tag{10}$$

since $0<R_n'<1-r$, it follows from (9) that

$$\frac{1}{1+r}<\rho_n<1. \tag{11}$$

Introducing ρ_n in Eqs. (7) and (8), these take the form

$$T_{n+1}=\frac{t}{1-r^2}\cdot\frac{T_n}{\rho_n}, \tag{12}$$

$$\rho_n-\rho_{n+1}=\frac{r^2}{(1-r^2)^2}\cdot\frac{T_n^2}{\rho_n}, \tag{13}$$

From these, we form a difference equation of the second order for ρ_n by eliminating T_n in the following manner: in (13), replace n by $n+1$ and in the result, substitute the value of T_{n+1} from (12), whence

$$\rho_{n+1}-\rho_{n+2}=\frac{r^2}{(1-r^2)^2}\cdot\frac{T^2{}_{n+1}}{\rho_{n+1}}=\frac{t^2r^2}{(1-r^2)^4}\cdot\frac{T_n{}^2}{\rho_{n+1}\rho_n{}^2}\ .$$

In the last expression, we substitute the value of $T_n{}^2$ taken from (13) obtaining

$$\rho_{n+1}-\rho_{n+2}=\frac{t^2}{(1-r^2)^2}\cdot\frac{\rho_n-\rho_{n+1}}{\rho_{n+1}\rho_n}=\frac{t^2}{(1-r^2)^2}\left(\frac{1}{\rho_{n+1}}-\frac{1}{\rho_n}\right)\ .$$

Transposing terms, we obtain the difference equation of the second order

$$\rho_{n+2}+\frac{t^2}{(1-r^2)^2}\cdot\frac{1}{\rho_{n+1}}=\rho_{n+1}+\frac{t^2}{(1-r^2)^2}\cdot\frac{1}{\rho_n}\ , \tag{14}$$

which shows that the expression to the right remains unchanged in value when n is increased by unity. Starting with $n=0$, and increasing it by a unit at a time, it follows that the right hand member of (14) has the same value for any n as for $n=0$, so that

$$\rho_{n+1}+\frac{t^2}{(1-r^2)^2}\cdot\frac{1}{\rho_n}=\rho_1+\frac{t^2}{(1-r^2)^2}\cdot\frac{1}{\rho_0}\ ,$$

and calculating the expression to the right by means of (10), we find

$$\rho_{n+1}+\frac{t^2}{(1-r^2)^2}\cdot\frac{1}{\rho_n}=1+\frac{t^2}{1-r^2}\ . \tag{15}$$

This difference equation of the first order is thus a first integral of (14), and is in its turn reduced to a directly integrable linear difference equation in the following manner. From (11) it is seen that ρ_n is positive, and from (13) that $\rho_n>\rho_{n+1}$. The sequence $\rho_0, \rho_1, \ldots, \rho_n, \ldots$ is thus decreasing toward a limit ρ:

$$\lim_{n\to\infty}\rho_n=\rho\ , \tag{16}$$

and (11) shows that

$$\frac{1}{1+r}\leqq\rho<1\ . \tag{17}$$

From (15) and (16) it is seen that ρ satisfies the equation

$$\rho+\frac{t^2}{(1-r^2)^2}\cdot\frac{1}{\rho}=1+\frac{t^2}{1-r^2}\ , \tag{18}$$

and solving this quadratic in ρ,

$$2(1-r^2)\rho=1+t^2-r^2\pm\sqrt{(1+t^2-r^2)^2-4t^2}\ .$$

To determine the sign of the radical, we observe that $t<1-r$ by (1), so that (17) gives

$$>\frac{t}{1-r^2}\,; \tag{19}$$

on the other hand, the product of the roots of (18) equals $t^2/(1-r^2)^2$, and consequently (19) shows that the second root of (18) is less than $t/(1-r^2)$. Hence ρ is the greater of the two roots of (18) and corresponds to the plus sign before the radical. Resolving the expression under the radical sign into factors, we thus obtain

$$2(1-r^2)\rho=1+t^2-r^2+\sqrt{(1+t+r)(1+t-r)(1-t+r)(1-t-r)}\;. \tag{20}$$

As $n\to\infty$, R_n tends toward a limit R, which equals $r+(1-r^2)(1-\rho)/r$ by (5) and (9), so that, according to (20),

$$R=\frac{1}{2r}\left[1-t^2+r^2-\sqrt{(1+t+r)(1+t-r)(1-t+r)(1-t-r)}\,\right]\;. \tag{21}$$

An expression for this R, which is the reflection in an infinite number of equally spaced parallel planes, was found in an entirely different way by K. W. Lamson[1] in form of an infinite series, the sum of which was shown by the author to be (20).[2]

Returning to Eq. (15), we subtract from it Eq. (18), obtaining

$$\rho_{n+1}-\rho=\frac{t^2}{(1-r^2)^2}\left(\frac{1}{\rho}-\frac{1}{\rho_n}\right)\,;$$

making the substitution

$$\rho_n=\rho\left(1+\frac{1}{\omega_n}\right), \tag{22}$$

the preceding equation becomes

$$\frac{\rho}{\omega_{n+1}}=\frac{t^2}{(1-r^2)^2}\cdot\frac{1}{\rho}\cdot\frac{1}{\omega_n+1}\,,$$

and writing

$$\mu=\frac{1-r^2}{t}\rho\,, \tag{23}$$

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[1] K. W. Lamson, Physical Review, N. S. **17**, 624 (1921), Eqs. (2) and (3).

[2] Lamson, l.c. Eq. (5). This formula contains two misprints: the minus sign between t^2 and r^2 should read plus, and a minus sign should be inserted between r^2 and the square root. For the proof, see T. H. Gronwall, Annals of Mathematics, ser. 2, **23**, 282 (1922).

so that $\mu > 1$ by (19), this reduces to the linear difference equation in ω_n:

$$\omega_{n+1} = \mu^2(\omega_n + 1) \ . \tag{24}$$

This may be written

$$\omega_{n+1} + \frac{\mu^2}{\mu^2 - 1} = \mu^2 \left(\omega_n + \frac{\mu^2}{\mu^2 - 1} \right) ,$$

and this last equation is integrated immediately, giving

$$\omega_n + \frac{\mu^2}{\mu^2 - 1} = \mu^{2n} \left(\omega_0 + \frac{\mu^2}{\mu^2 - 1} \right) .$$

Since $\rho_0 = 1$ by (10), we have $\omega_0 = \rho/(1-\rho)$ by (22), so that finally

$$\omega_n + \frac{\mu^2}{\mu^2 - 1} = \left(\frac{\rho}{1-\rho} + \frac{\mu^2}{\mu^2 - 1} \right) \mu^{2n}. \tag{25}$$

Having thus determined ω_n explicitly as a function of r, t and n, we obtain R_n by the combination of (5), (9), and (22):

$$R_n = \frac{1}{r} - (1 - r^2)\rho \left(1 + \frac{1}{\omega_n} \right) . \tag{26}$$

For T_n, we find from (13) and (22)

$$\frac{r^2}{(1-r^2)^2} T_n^2 = \rho^2 \cdot \frac{1+\omega_n}{\omega_n} \cdot \frac{\omega_{n+1} - \omega_n}{\omega_n \omega_{n+1}} ,$$

or replacing ω_{n+1} by its expression from (24) and using (23),

$$T_n^2 = \frac{t^2}{r^2} \cdot \frac{(\mu^2 - 1)\omega_n + \mu^2}{\omega_n^2} . \tag{27}$$

5. *Approximate formulas for calculating r and a from experimental values of R and T_n.* In experimental work, it is possible to determine the reflection in a section of the material of sufficient thickness to allow us to regard the number N of planes contained in it as infinite, that is, R is measured. Then the transmission T_n is measured in a section as thin as possible (n of the order 10^5). Now both r and a are very small (of the order of magnitude 10^{-6}), and a is several times less than r. This suggests writing

$$a/r = \alpha \ , \tag{28}$$

so that $\alpha < 1$, and expanding ρ, μ etc. in powers of r. By (1) and (28) we have

$$t = 1 - (1 + \alpha)r \ . \tag{29}$$

whence

$$t^{-1}=1+(1+\alpha)r+(1+\alpha)^2r^2+(1+\alpha)^3r^3+\cdots\,,$$
$$t^{-2}=1+2(1+\alpha)r+3(1+\alpha)^2r^2+4(1+\alpha)^3r^3+\cdots\,. \qquad (30)$$

It is convenient to introduce the notation

$$\beta=\sqrt{\alpha(2+\alpha)}\,,\qquad (1+\alpha)^2=\beta^2+1\,, \qquad (31)$$

and from (29) we find

$$\sqrt{(1+t+r)(1+t-r)(1-t+r)(1-t-r)}=2\beta r\,\sqrt{1-[(1+\alpha)r-\tfrac{1}{4}\beta^2r^2]}\,,$$

or expanding by the binomial theorem

$$\sqrt{(1+t+r)(1+t-r)(1-t+r)(1-t-r)}$$
$$=2\beta r\left[1-\frac{1}{2}(1+\alpha)r-\frac{1}{8}r^2-\frac{1}{16}(1+\alpha)r^3-\cdots\right], \qquad (32)$$

whence by (20) and (21)

$$(1-r^2)\rho=1-(1+\alpha-\beta)r-\frac{\beta}{2}(1+\alpha-\beta)r^2-\frac{1}{8}\beta r^3-\cdots\,, \qquad (33)$$

$$R=1+\alpha-\beta+\frac{1}{2}\beta(1+\alpha-\beta)r+\frac{1}{8}\beta r^2+\cdots\,. \qquad (34)$$

In the last equation, it is sufficient to retain the constant term, so that $R=1+\alpha-\sqrt{\alpha(2+\alpha)}$, whence, solving for α,

$$\alpha=(1-R)^2/2R\,,\qquad \beta=1+\alpha-R=(1-R^2)/2R\,. \qquad (35)$$

This determines α in terms of the measured R.[3] To find r from the measured T_n, we expand μ in powers of r by means of (23), (30) and (33):

$$\mu=1+\beta r+\tfrac{1}{2}\beta(1+\alpha+\beta)r^2+\cdots\,, \qquad (36)$$

whence

$$\frac{\mu^2}{\mu^2-1}=\frac{1}{2\beta r}\left[1-\frac{1}{2}(1+\alpha-2\beta)r+\cdots\right]. \qquad (37)$$

From (33) and (37) it follows that

$$\frac{\rho}{1-\rho}+\frac{\mu^2}{\mu^2-1}=\frac{1}{r}\left(1+\alpha+\beta+\frac{1}{2\beta}+\cdots\right), \qquad (38)$$

---

[3] Actually, (34) gives α as a power series in r, the constant term being (35), and the next term $(1-R^2)^2/8R^2\cdot r$ which is small enough to be neglected.

where the terms not written out contain the first and higher powers of r. Solving (27) for ω_n, we find

$$\omega_n = \frac{t^2}{2r^2T_n^2}\left[\mu^2 - 1 + \sqrt{(\mu^2-1)^2 + 4\mu^2 r^2 T_n^2 t^{-2}}\,\right],$$

where the radical is taken with the plus sign, since ω_n is positive by (24). Using (36) and (30), we find that the lowest term in r inside the bracket is $(2\beta + 2\sqrt{\beta^2 + T_n^2})r$, so that, with the aid of (37),

$$\omega_n + \frac{\mu^2}{\mu^2-1} = \frac{1}{r}\left(\frac{\beta + \sqrt{\beta^2 + T_n^2}}{T_n^2} + \frac{1}{2\beta} + \cdot\cdot\cdot\right). \tag{39}$$

Dividing (39) by (38), taking the natural logarithm on both sides and expanding the logarithm of the right hand member in powers of r, we find

$$\log \frac{\omega_n + \dfrac{\mu^2}{\mu^2-1}}{\dfrac{\rho}{1-\rho} + \dfrac{\mu^2}{\mu^2-1}} = \log \frac{\dfrac{\beta + \sqrt{\beta^2 + T_n^2}}{T_n^2} + \dfrac{1}{2\beta}}{1 + \alpha + \beta + \dfrac{1}{2\beta}} + \cdot\cdot\cdot\cdot.$$

By (25), the expression to the left equals $2n \log \mu$, and since $\log \mu = \beta r + \cdot\cdot\cdot$ by (36), we finally find, retaining only the lowest powers of r on either side,

$$r = \frac{1}{2n\beta}\cdot\log \frac{\dfrac{\beta + \sqrt{\beta^2 + T_n^2}}{T_n^2} + \dfrac{1}{2\beta}}{1 + \alpha + \beta + \dfrac{1}{2\beta}}. \tag{40}$$

Since α and β are known by (35), this determines r in terms of the measured T_n, and finally (28) and (29) give $a = \alpha r$, $t = 1 - (1+\alpha)r$.

EVIDENCE FROM CRYSTAL STRUCTURES IN REGARD TO ATOMIC STRUCTURES[1]

By Maurice L. Huggins[2]

Abstract

The distribution of valence electrons in the diamond and similar crystals.—Because of the cubical symmetry, the equivalent scattering power of all the atoms, and the absence of pyro- and piezo-electric effect, the atoms in the diamond cannot be held together as a result of the transfer of electrons from atom to atom. Symmetry requirements also eliminate any cubical arrangement of electrons or orbits around each atom. The diamagnetism of H_2 and of most organic compounds eliminates rotations of two electrons or orbits in the same direction about each atomic center-line as a means of holding the atoms together. Similar structures and numbers of valence electrons, together with interatomic distance comparisons, indicate that the atoms in BeO, ZnO, ZnS, CdS, AgI, etc., are held together in a manner similar to that in the diamond. If so, there cannot be four electrons rotating around each atomic kernel in the diamond, for Zn^{--}, Ag^{---}, O^{++} etc., are chemically impossible. It is not possible for two electrons to be rotating about each two adjacent atomic kernels in crystals of NaCl, MgO, CdO, AgBr, etc., and since chemically and physically these are not very different from BeO, CdS, AgI, etc., the bonds in the last named crystals and so in the diamond are probably not of this type. The conclusion is therefore reached that in the diamond and crystals of similar structure, the electrons are in pairs at tetrahedron corners around each atom, each pair being held jointly by two atoms. This is as predicted from the Lewis theory of valence. A study of the other known crystal structures leads to the conclusion that in general the valence shells of electro-negative atoms are tetrahedra of electron pairs rather than cubes of single electrons.

THIS paper is an attempt to show that important conclusions concerning the ways in which the valence electrons are arranged may be reached from a careful analysis of the structures of some of the simplest crystals.

The diamond. The arrangement[3] of atoms in this substance is pictured in Figs. 1 and 5. Each carbon atom is surrounded by four others placed around it as are the four corners of a regular tetrahedron around its center. All the atoms are equivalent, both as regards their positions in the structure and their ability to scatter x-rays. The symmetry of the structure, as shown by both the crystallographic and the x-ray data, is that of the cubic or isometric system.

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[1] Some of the material given in this paper has been presented at meetings of the American Physical Society and the American Chemical Society. For abstracts, see Phys. Rev., **21,** 379 (1923) and Science, **57,** 534 (1923). The electron distributions arrived at were proposed by the author in the J. Am. Chem. Soc. **44,** 1841 (1922).

[2] National Research Fellow.

[3] See Wyckoff, "The Structure of Crystals," Chem. Cat. Co., New York, 1924, for references to the crystal structure work.

There are four valence electrons per atom; our problem is to determine, if possible, how they are distributed.[4] The tetrahedral arrangement around each atom, the stability of the diamond toward disruption by heat or chemical action, its low electrical conductivity, etc., suggest that the atoms in this crystal are held together in the same manner as the carbon atoms in "saturated" organic compounds.[5] The theories which have been proposed for the nature of such a union may be divided into two classes, (1) those assuming the transfer of electrons from atom to atom,[6] the individual carbon atoms being represented as ${}^{+}_{+}C^{+}_{+}$, ${}^{+}_{+}C^{+}_{-}$,

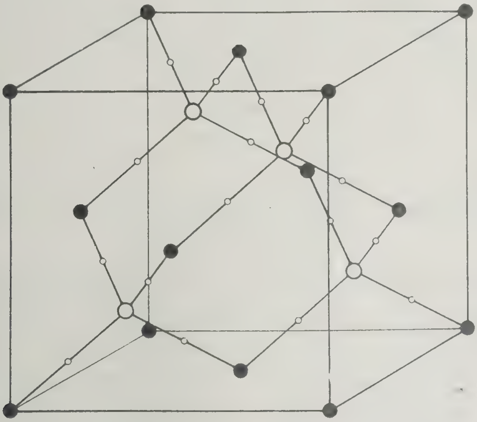

Fig. 1. Unit cube of the diamond, cubic ZnS, etc. In the diamond all atoms are of carbon and the electron pairs, represented by the small circles, are at the mid-points of the atomic centerlines, as shown. In ZnS the Zn atoms are in the positions represented by the large dots, the S atoms are in those represented by the large circles, and the electronpairs are on the centerlines between atoms, but closer to the sulfur than to the zinc.

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[4] It would also be of interest to learn how the two K electrons of each atom are placed, but the evidence at hand is insufficient to enable us to do this. The symmetry and x-ray requirements are met if they are so close to the nuclei as not to affect appreciably the symmetry of the arrangement of valence (L) electrons, and either are oriented relative to their nuclei in a random way throughout the crystal or are regularly distributed in a large unit having cubic symmetry.

[5] Such interatomic distance data as are at present available for crystals of organic compounds are also in agreement with this idea. If correct, then the conclusions to be drawn regarding the type of atom-bonding in the diamond are also applicable to the bonds within organic molecules.

[6] Thomson, "The Corpuscular Theory of Matter," Scribner, New York, 1907; Falk and Nelson, J. Am. Chem. Soc. **32,** 1637 (1910); Fry, Zeits. f. Phys. Chem. **76,** 385 (1911); J. Am. Chem. Soc. **34,** 664 (1912); Stieglitz, ibid, **44,** 1293 (1922).

${}^{+}_{-}\mathrm{C}^{+}_{-}$, ${}^{+}_{-}\mathrm{C}^{-}_{=}$, or ${}^{-}_{-}\mathrm{C}^{-}_{-}$; and (2) those postulating the sharing of electrons between atoms.[7]

Considering now the first of these classes, if the atoms in the diamond were half ${}^{+}_{+}\mathrm{C}^{+}_{+}$ and half ${}^{-}_{-}\mathrm{C}^{-}_{-}$ they would not have equivalent scattering powers, for those of the first kind would have but two electrons each, while those of the latter would have ten. Furthermore, the [111] faces of the crystal would be electrically polar, the layers of atoms parallel to these faces being alternately positive and negative and spaced as indicated in Fig. 2. This would be made manifest by the presence of pyro-electric and piezo-electric effects, as in ZnS, for instance. The same objections apply to a structure consisting of ${}^{+}_{+}\mathrm{C}^{+}_{-}$ and ${}^{+}_{-}\mathrm{C}^{-}_{-}$ atoms, arranged so that each carbon-carbon bond is positive at one end and negative at the other; there is also the additional objection that the distribution of charges would have the symmetry of the trigonal system rather than that of the cubic or regular system. This would result not only in displacement of the atomic centers in the direction of the three-fold symmetry axis, but in irregular growth, unsymmetrical etch figures, interference figures (produced by polarized light) indicative of the lower symmetry, etc. If all the atoms in the crystal were ${}^{+}_{-}\mathrm{C}^{+}_{-}$, held together by electrostatic forces concentrated at the "ends of the bonds," the crystal would have tetragonal symmetry and the [001] faces would be polar, as the positive ends of all the atoms would be turned in the same direction. We thus arrive at our first conclusion, that *the atoms in the diamond are not held together as a result of the transfer of electrons from one atom to another.* This must be true whether the electrons are in or vibrating about fixed positions in the atoms, or are revolving in orbits.

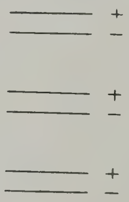

Fig. 2. Spacing of [111] planes in ZnS (also in the diamond, if the atoms were charged).

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[7] Lewis, J. Am. Chem. Soc. **38,** 762 (1916); "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., New York, 1923; Bohr, Phil. Mag. **26,** 857 (1913).

According to the electron-sharing theory, which chemists[8] have found exceedingly useful in accounting for the properties of substances containing non-polar bonds, the kernel of an electronegative atom tends to be surrounded by a valence shell containing eight electrons, and in order to accomplish this result it bonds with other atoms, two electrons (or electron orbits) shared between two atoms constituting a typical "single bond." The eight electrons of a complete shell were at first represented as at corners of a cube, but, in order to account for the triple bond of organic chemistry and for other reasons, the "cubical atom" was later abandoned in favor of the "tetrahedral atom," in which the valence electrons are assumed to be drawn together in pairs.[9]

If each atom in the diamond had a valence shell consisting of a cube of single electrons or electronic orbits (Fig. 3), the crystal would have tetragonal symmetry, for the arrangement in the direction of one of the crystal axes would be different from that in the direction of each of the other two axes. The ratio of the unit distances would be $1:1:\sqrt{2}$, rather than $1:1:1$, as is actually the case. *No cubical arrangement of electrons or electron orbits around each atom, with two electrons or orbits shared between each two adjacent atoms, could give a structure for the diamond having the symmetry of the cubic system.*

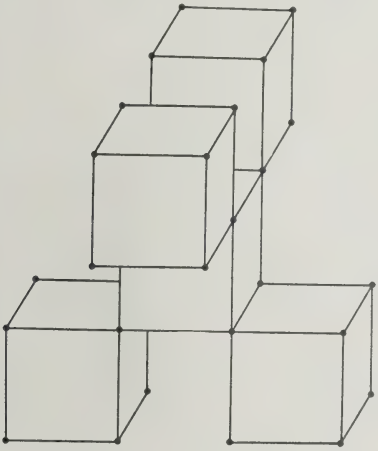

Fig. 3. Cubes edge to edge in a pseudo-diamond type of structure having tetragonal symmetry. The small dots represent single valence electrons.

The minimum elements of symmetry which a crystal must possess in order to belong to the cubic system[10] are four three-fold symmetry axes and three two-fold symmetry axes. As the observations used to determine the symmetry of crystals—the symmetry of the diffraction effects with light and with x-rays, the rates of growth and solution in different directions, etc.—depend largely (in case of the diamond at least) on the distribution of the valence electrons, we may say with certainty that their distribution must either possess the elements of symmetry just mentioned or there must be a randomness in the arrangement which statistically will produce the observed effects. Inspection of the arrangement of atomic centers in the diamond shows that a distribution of *pairs* of electrons tetrahedrally about each atomic kernel satisfies the symmetry requirements just mentioned, *provided both electrons of each pair are on, or distributed in a random manner about, the straight line connecting the two nearest atomic centers.* The corresponding requirements which must be satisfied by a distribution of electron *orbits* in the diamond may be stated as follows: *Fixed (non-precessing) orbits, other than circular orbits in planes normal to the three-fold axes, are impossible, unless oriented in a random manner about these axes. If there are electron rotations or orbital precessions, they cannot be synchronized with each other throughout the crystal.* If the synchronization were such as to produce one true three-fold symmetry axis there could be no other similar axes in the crystal. In other words, it is impossible to build up any crystal having the cubic symmetry which the diamond is known to possess with *fixed* orbits or *synchronized* precessions or rotations.

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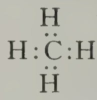
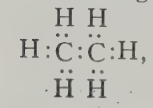
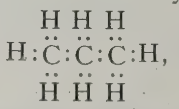
[8] Lewis, Ref. 7; Langmuir, J. Am. Chem. Soc. **41,** 868, 1543 (1919); **42,** 274 (1920); Latimer and Rodebush, ibid. **42,** 1419 (1920); Huggins, ibid. **44,** 1607 (1922).

[9] Lewis, Ref. 7; Huggins, J. Phys. Chem. **26,** 601 (1922).

[10] See any good book on crystallography.

Considering now the types of orbital motions not ruled out by the arguments in the foregoing paragraphs, we might imagine adjacent carbon atoms to be held together as a result of rotations of electrons or of orbits about the atomic center-line in one of the ways represented in Fig. 4.[11] If the first were correct, though, and the same type of bonding exists in organic molecules, a large majority of the latter should be paramagnetic. A compound like methane,  $\mathrm{H}:\underset{\mathrm{H}}{\overset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{C}}}}}:\mathrm{H}$, we might expect to be diamagnetic, but it would seem very unlikely that in ethane,  $\mathrm{H}:\underset{\mathrm{H}}{\overset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{C}}}}}:\underset{\mathrm{H}}{\overset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{C}}}}}:\mathrm{H}$, or in propane,  $\mathrm{H}:\underset{\mathrm{H}}{\overset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{C}}}}}:\underset{\mathrm{H}}{\overset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{C}}}}}:\underset{\mathrm{H}}{\overset{\mathrm{H}}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{\mathrm{C}}}}}:\mathrm{H}$, for instance, the magnetic effect of each pair could be counterbalanced by the effects of the others. The same argument would of course also apply to molecular hydrogen, if the atoms were held together in the manner of Fig. 4A.[12]

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[11] Cf. Lewis, "Valence, Etc." (Ref. 7) p. 59.

[12] Cf. Bohr, Ref. 7.

Moreover, if the bonds in the diamond were of this type, there would be two kinds of atoms. In one all rotations would be clockwise, in the other counter-clockwise, as seen from the center of the atom. (If each atom contained both clockwise and counter-clockwise rotations, the crystal would have trigonal or tetragonal symmetry, as was shown would be the case if the atoms contained both plus and minus charges —${}^{+}_{-}C^{+}_{-}$ or ${}^{+}_{-}C^{-}_{-}$ and ${}^{+}_{+}C^{+}_{-}$.) Atoms of the first kind could only combine with those of the second kind, and vice versa. If they were held together as indicated in Fig. 4B, all the atoms in a single crystal would be of the same kind, having all the rotations (of the nearest valence electrons) clockwise, for instance, as viewed from the atomic center. There is of course no *a priori* reason for assuming that counter-clockwise atoms could not exist, but they would have to be in a different crystal, for only atoms of like rotational character could combine together. Either of these two hypotheses would lead to rather fantastic conclusions with regard to organic reactions, but further discussion of this subject is beyond the scope of this paper.

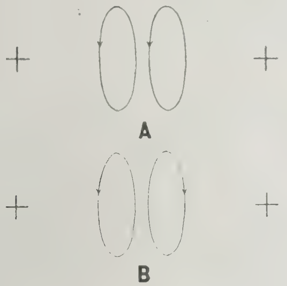

Fig. 4. Representing two types of rotations of valence electrons or orbits about atomic centerlines.

It might be noted in addition that from ordinary electromagnetic theory we should expect repulsion between two electrons of a pair rotating as in Fig. 4B. This would also be true, except in the case of ring electrons, if the electrons were rotating as in Fig. 4A.

In order to proceed further with the elimination of proposed types of interatomic bonds, we shall now consider other closely related structures.

Crystals having structures similar to that of the diamond. Silicon,[13] germanium,[3] and gray tin[3] have been found to have crystal structures of the same type as the diamond. Each of these elements is tetravalent and it seems reasonable to assume four valence electrons per atom and that the atoms are held together in the same way as are the carbon atoms in the diamond. Insofar as the chemical and physical properties of these substances are known, they are in accord with these conclusions. The binary compounds ZnS[3], $ZnSe$[14], $ZnTe$[15], HgS[16], $HgSe$[15] $HgTe$,[15] $CdTe$[15], $CuCl$[3], $CuBr$[3], CuI[3], AgI[3], and $AlSb$[17], also have the same type of structure, half of the atoms of course being of one kind and half of the other. In ZnS, for example, each zinc atom is surrounded by four sulfur atoms at corners of a regular tetrahedron and each sulfur similarly by four zinc atoms (Figs. 1 and 5).

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[13] Ref. 3. Küstner and Remy, Phys. Zeits. **24,** 25 (1923).

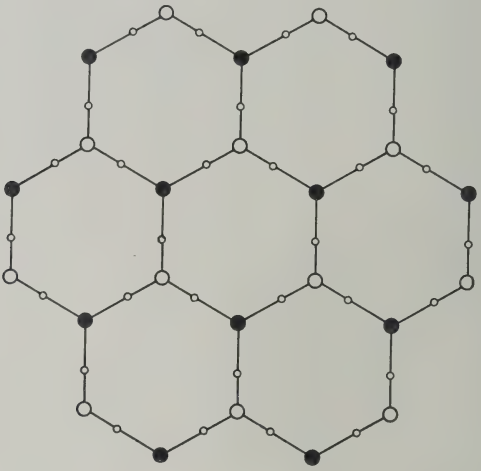

Fig. 5. Representing the distribution of atoms and electronpairs within each layer in crystals of the diamond, ZnS, and ZnO types. The large dots and large circles denote atoms in different planes. In the diamond, Si, etc., all atoms are of the same kind and the electronpairs (small circles) are midway between atomic centers: in ZnO, ZnS, etc., the dots represent atoms of one kind and the large circles those of another, the electronpairs being closer to one kind of atom than to the other, as shown. In crystals of either type each atom is also bonded to another, directly over or under it, in another layer.

A number of other binary compounds, namely AlN[18], BeO[3], ZnO[3], ZnS[3], $ZnSe$[15], CdS[19], $CdSe$[15], and AgI[3], possess structures which, although they have the symmetry of the hexagonal system, resemble the cubic structures just mentioned in that each atom is surrounded tetrahedrally by four others of opposite character (Cf. Fig. 5). This is probably also true of carborundum (SiC)[20].

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[14] Huggins, Phys. Rev. **21,** 211 (1923). Davey, ibid. **21,** 380 (1923).

[15] Huggins, Ref. 14.

[16] Huggins, Ref. 14. Kolkmeijer, Bijvoet and Karssen, Proc. Acad. Sci., Amsterdam, **27,** 390 (1924); Verslag Akad. Wetenschappen **33,** 327 (1924).

[17] Owen and Preston, Proc. Phys. Soc., **36,** 341 (1924).

[18] Ott, Zeits. f. Phys. **22,** 201 (1924).

[19] Ref. 3. Huggins, Ref. 14.

In the cubic structures listed above, the tetrahedron of atoms closest to any given atom *must* be regular; in the hexagonal crystals it is also very nearly regular (at least within a percent or two, approximately the limit of error of the experimental determinations). Moreover, in those cases (e.g. ZnS and AgI) in which the same chemical compound crystallizes in both ways, the distance between adjacent atoms (Table I) is almost identically the same in the two crystals.

TABLE I

Interatomic distances in various crystals

Crystal	Distance	Reference
C	1.54A	Bragg[3], Hull[3]
Si	2.34–2.36	Debye and Sherrer[3] Hull[3], Gerlach[3], Küstner and Remy[13]
Ge	2.43; 2.44	Kolkmeijer[3], Hull[3]
Sn	2.80	Bijl and Kolkmeijer[3]
SiC	1.90	Ott[20]
AlN	1.89	Ott[18]
AlSb	2.65	Owen and Preston[17]
BeO	1.65	McKeehan[3]
ZnS, cubic	2.34; 2.35	Gerlach[3], Bragg[3]
ZnS, hexagonal	2.33; 2.36	Aminoff[3]; from density=3.98 (Mourlot[21])
ZnSe	2.45; 2.43	Davey[3]; from density=5.40 (Margottet[22])
ZnTe	2.53	From density =6.34 (Margottet[22])
CuCl	2.32; 2.38	Davey[3]; Wyckoff and Posnjak[3]
CuBr	2.49; 2.52	Davey[3]; Wyckoff and Posnjak[3]
CuI	2.61; 2.63; 2.64	Aminoff[3]; Davey[3]; Wyckoff and Posnjak[3]
AgI, cubic	2.81; 2.83	Wilsey[3]; Davey[3]
AgI, hexagonal	2.81	Aminoff[3]; Wilsey[3]

This, together with the further fact that the physical and chemical properties of the two forms are all almost exactly the same, shows that the atoms in both must be held together in the same way.

If we follow Thomson,[6] Lewis,[7] Kossel,[23] Bury,[24] Bohr,[25] Huggins,[9] Stoner,[26] and others in assigning one valence electron to each atom of an element in Group I of the periodic table, two electrons to each atom of an element in Group II, etc., we find that in all of these crystals there is an average of four electrons per atom, the same as in the diamond, Si, Ge, and Sn. Moreover, as shown by Table I, pairs of crystals

[20] Ott, Naturwissenschaften **13,** 76 (1925). See also Ref. 3.

[21] Mourlot, Ann. d. chim. Phys. **17,** 534 (1899).

[22] Margottet, Compt. rend. **84,** 1293 (1877).

[23] Kossel, Ann. der Physik, **49,** 229 (1916).

[24] Bury, J. Am. Chem. Soc. **43,** 1602 (1921).

[25] Bohr, Zeits. f. Physik **9,** 1 (1922).

[26] Stoner, Phil. Mag. **48,** 719 (1924).

with similar physical and chemical properties (diamond and BeO, Ge and ZnSe, Sn and AgI, and SiC and AlN) have nearly the same interatomic distances.

It seems highly probable then that *the atoms in all of these compounds are held together in a way which is not radically different from that in the diamond.* Any theory of the nature of the bonds between the atoms must be applicable to all of these compounds without necessitating any abrupt change from one type of bond to another. *It would therefore seem very unlikely that in zinc sulfide, for instance, all the valence electrons are in rotation in orbits enclosing the sulfur kernel with none enclosing the zinc kernel*, for such a distribution (of *all* the electrons about *half* the atoms) was shown to be impossible in the diamond, and an abrupt change would be necessitated in going from such a structure to one in which four electrons were rotating around each kernel. By similar reasoning *we must consider extremely improbable any arrangement of four electrons rotating about each atomic kernel* in the diamond, for such a structure for ZnS, BeO, or AgI would require such chemically absurd ions as Zn^{--}, Ag^{---}, O^{++} etc. Moreover, no structure placing but two electrons about each electropositive atom and six about each electronegative atom (in ZnS or BeO) is possible, because a corresponding electron distribution in the diamond could not be correct.

Crystals having the sodium chloride type of structure. The following compounds have been found to have the type of atomic arangement pictured in Fig. 6: LiF, LiCl, LiBr, LiI, NaF, NaCl, NaBr, NaI, KF, KCl, KBr, KI, RbCl, RbBr, RbI, CsF, MgO, MgS, CaO, CaS, CaSe, SrO, SrS, SrSe, BaO, BaS, BaSe, MnO,[27] MnS, CdO, NiO, CoO, PbS, AgCl, and AgBr.

If we again assume current theories[28] in regard to the number of valence electrons to be correct, we find in each case,[29] as before, an average of four per atom. In these crystals, however, there are *six* equivalent electronegative atoms around each electropositive atom and vice versa, and it is not structurally possible for the atoms to to be held together by electrons rotating in orbits enclosing two nuclei. If the bonds between atoms were of this type in the crystals having structures like the diamond, ZnS and ZnO, we should then expect very decided differences in properties between the two classes of substances. When we compare the properties[30] of BeO and MgO, of CdO and CdS, or of

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[27] Levi, Gazz. chim. ital., **54,** 704 (1924).

[28] Ref. 6, 7, 23, 24, 25, 26.

[29] Except, perhaps, in PbS.

[30] See any standard work on inorganic chemistry.

AgBr and AgI, we find no such marked differences. *This observation eliminates from further consideration any structure*, for any of the crystals so far discussed, *in which the atoms are held together by valence electrons in rotation about two atomic centers.*

We have then no alternative but to conclude that, provided the arguments used in the foregoing analysis are valid, *the valence electrons in the diamond and crystals of similar structure*, including those of the zinc oxide type, *are in pairs at tetrahedron corners around each atomic kernel, each electron pair being held jointly by two atoms.* Whether the electrons are in, or oscillating about, equilibrium positions on the atomic centerlines, or are ring electrons or electrons rotating in orbits about these centerlines (in the relative directions indicated in Fig. 4B) need not be further discussed at this time.

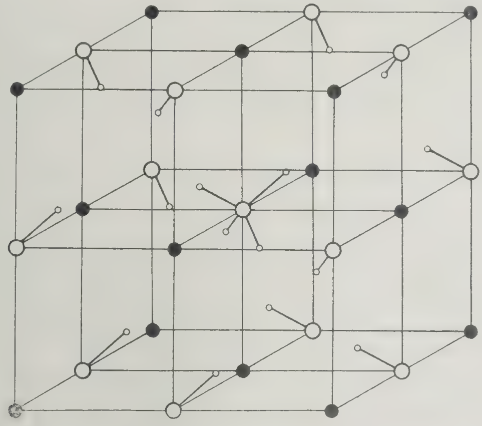

Fig. 6. Unit cube of the sodium chloride structure, showing the probable distribution of the valence electronpairs. The large dots represent sodium kernels and the large circles chlorine kernels. Atoms of either kind, considered separately, are at the points of a face-centered cubic lattice.

It has not been shown whether the valence electrons in crystals of the sodium chloride type are in pairs at tetrahedron corners, or singly at cube corners, around the kernels of the electronegative atoms. Certainly, if we had only crystals of this type to consider, the cubical arrangement would seem more likely than the tetrahedral, but the fact that in all the other crystals discussed in this paper and in many more to be dealt with in another article[31] the kernel of each electronegative atom must be surrounded by a tetrahedron of electronpairs makes it seem very probable that this is also the case in these crystals (Fig. 6).

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[31] Soon to be published.

As the valence electrons are surely much more tightly held by the kernels of the electronegative atoms (within the valence tetrahedra) than by those of the electropositive atoms, it is often convenient, and an approximation to the truth, to speak of the structure as composed of electropositive and electronegative "ions." Similarly we may speak of the "ions" of beryllium and oxygen in a crystal of BeO, but in either case it should be understood that the valence electrons have not passed *completely* from one atom to another but are mutually held by two or more atoms, also that all degrees of "ionization" (or better, "polarity") are possible, these substances and the diamond being extreme cases.

Other crystals. A study[31] of other crystals of known structure has resulted in the following conclusions:

(1) *In all those which contain electronegative atoms,* excepting only $CsICl_2$, graphite, and certain carbonates and nitrates, *the arrangement is such as to permit a valence shell of 8 electrons around the kernel of each electronegative atom.*

(2) In those which contain electronegative atoms adjacent to each other, excepting only $C(CH_2OH)_4$ and the crystals just mentioned as exceptions to the preceding generalization, valence shells consisting of tetrahedra of electronpairs are possible in full accord with all available data, while cubic valence shells are in FeS_2, MnS_2, Se and Te improbable and in all other cases impossible.

(3) In those containing both electropositive and electronegative atoms, with the latter not adjacent to each other, a comparison of the structures obtained on the assumption of tetrahedral valence shells with those obtained on the assumption of cubical valence shells favors the former as the more probable in nearly every case.

(4) In crystals of the metals, the prevailing tendency seems to be for each atom to surround itself by as many others as possible, the number of valence electrons and the orienting tendencies of the atomic kernels being of minor importance.

In view of the above, it would seem reasonable to assume a tetrahedron of electronpairs as the valence shell of each electronegative atom, whenever such an assumption is not in conflict with x-ray or other evidence. The probable electronic distributions so obtained will be dealt with in detail in another paper.[31]

The Cause of Pairing. Although the author believes that the evidence given in this paper conclusively proves the existence of electronpairs in atomic shells, he is not able to give any satisfactory reason for their existence. There seem to be two alternatives; either there must be an attractive force between electrons at small distances, or the repulsion between electrons must rapidly decrease with decrease in distance, for distances less than a certain value. The latter alternative would not require electronpairing except in atomic shells, but would qualitatively at least account for the formation of pairs and for the grouping of electrons into distinct shells.

In conclusion the author wishes to express his thanks to Professor D. L. Webster of Stanford University for his valuable criticism.

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April 10, 1925.

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BAND SERIES IN INFRA-RED ABSORPTION SPECTRA OF ORGANIC COMPOUNDS. I

By Joseph W. Ellis

Abstract

The frequencies of a series of outstanding absorption bands characteristic of organic liquids, previously attributed by the author to vibrations between atoms of a carbon-hydrogen pair, are shown to fit the equation,

$$\nu_n \cdot 10^{-12} = 47.37n - 0.783n^2,$$

where $n=1, 2, \ldots\ldots, 10$. Many of the bands of secondary intensity in the spectra of compounds containing a carbon-carbon bond have their frequencies expressed by

$$\nu'_n \cdot 10^{-12} = 10.71n.$$

where $n=1, 2, \ldots\ldots, 28$. Practically all other bands observed below 7μ in such spectra can be accounted for by combinations of low frequency members of these two series, $\nu_c = \nu_m + \nu_n'$. Measurements on bands occurring between 2μ and 3μ were made from records obtained with a new registering spectrograph. A number of such spectra are shown.

FOR a decade and a half following the publication by Coblentz[1] of his extensive monograph on infra-red absorption and emission spectra, comparatively little work was done in infra-red spectroscopy, especially in the study of absorption by organic compounds. During this period, however, Weniger[2] published his results of an investigation of a number of alcohols; Johnson and Spence[3] studied a number of aniline dyes, and Stang[4] investigated the absorption of naphthalene and some of its derivatives dissolved in carbon disulfide and carbon tetrachloride.

The origins of the great number of absorption bands observed in such investigations have remained practically unexplained. Puccianti,[5] in a short but accurate and important investigation, discovered a band near 1.71μ occurring in all of the fifteen carbon-hydrogen compounds which he had examined, and attributed it to a C-H group. Coblentz[1] had observed a few bands bearing multiple wave-length relationships to be characteristic of groups of compounds, and assigned as the origin of such bands groups within the molecule, as the alkyl groups CH_2 and CH_3.

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[1] Coblentz, "Investigations of Infra-red Spectra" (1905).

[2] W. Weniger, Phys. Rev. **31**, 388 (1910).

[3] Johnson and Spence, Phys. Rev. **5**, 349 (1915).

[4] Stang, Phys. Rev. **9**, 542 (1917).

[5] Puccianti, Nuovo Cim **11**, 141 (1900); Phys. Zeits. **1**, 48 (1899); **1**, 494 (1900).

Interest is again being aroused in the study of absorption spectra of organic compounds with a view to explaining the numerous bands which characterize them. Lecomte,[6] in a series of short articles, gives results, obtained with a Hilger infra-red wave-length spectrometer, of an investigation of many types of compounds. He concludes that the bands originate from vibrations within the molecule rather than of the molecule as a whole. In particular, he concludes that absorption due to the carbon atoms is but little dependent upon the type of carbon chain. Bell[7] has recently carefully determined the absorption between 2μ and 12μ of aniline and ten alkyl anilines, and finds that, among the numerous bands which occur, one at 2.8μ is characteristic of the amino group. Two years ago the writer[8] published in this journal the results of an investigation of the absorption spectra of thirty-one organic liquids to 2.5μ, obtained with a self-registering flint glass spectrograph of high dispersion. The liquids studied were benzene, toluene, p-xylene, mesitylene, pentane, hexane, heptane, octane and several halogen derivatives of methane, ethane, propane and butane. The investigation showed great similarities among these spectra. Márton[9] has just published the results of an investigation, which he began before the above work was published, in which he independently arrived at some of the author's earlier conclusions, which will be reviewed later in this article.

An examination of the spectrum curves presented in both the early and later investigations reveals two facts which suggest that the absorption bands may be arranged in series originating in the longer wavelength region, whose members suffer gradual diminution of intensity and increasingly shorter wave-length separations as the series progresses toward the limits of the visible spectrum. These facts are:

1. For investigations in the region between 15μ and 3μ best results are obtained when absorbing thicknesses of 0.1 mm or less are used; for the regions between 3μ and 2μ and 2μ and 1μ, cells of 1 mm and 10 mm respectively yield best results; while to bring out clearly the bands between 1μ and the visible red, cells of about 100 mm thickness have to be used.

2. There are relatively fewer bands in the longer than in the shorter wave-length region.

[6] Lecomte, Compt. Rend. **178,** pp. 1530, 1698, 2073 (1924); **180,** 825 (1925).

[7] F. K. Bell, J. Am. Chem. Soc. **47,** 2192 (1925).

[8] Ellis, Phys. Rev. **23,** 48 (1924).

[9] Márton, Zeits. f. Phys. Chem. **117,** 97 (1925).

The complexity of the absorption curves increases more with an increase in the number of distinct types of atoms within the absorbing molecule than with the general complexity, or size, of the molecule itself. This suggests that the origin of the different absorption bands may be traced to definite atoms, or pairs of atoms, as absorbing centers.

A theory of infra-red absorption which would explain all of the bands of very long wave-length as originating from pure rotational effects of the molecule and all of the shorter wave-length bands as due to a combination of rotations and linear vibrations has met with some success in the cases of some relatively simple gas molecules. The series of regularly spaced bands in the long wave-length region of water vapor spectra found by Rubens[10] and Fr. von Bahr[11] has been considered an example of the effects of pure rotation of a molecule in the absorption of radiant energy. A second, and more recent, example of a pure rotation spectrum is the series of regularly spaced absorption bands of HCl found by Czerny[12] between 40μ and 80μ. Such rotations have been quantized, and infra-red bands due to them are assumed to originate from discrete changes among the possible states of rotation, the angular momenta of these states bearing integral ratios to one another.

The second type of absorption, first proposed by Bjerrum,[13] predicts that bands in the short wave-length region should be double, and that when studied with a spectroscope of high resolving power each branch should appear made up of equally spaced lines, whose separations should be equal to those of longer wave-length bands of the purely rotational type. Such serrated bands had already been observed by Rubens[10] and Fr. von Bahr[11] in the cases of water vapor and HCl gas, but the first precision measurements were made on the former gas by Sleator,[14] and in the case of HCl and also HF and HBr, by Imes.[15] The separation of Czerny's long wave-length bands for HCl are equal to those found by Imes in the fine line structure of the near infra bands, thus confirming, in this case, Bjerrum's theory. Bands of the latter type have recently been measured in the spectrum of ammonia by Spence,[16] and in the spectrum of methane by Cooley.[17]

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[10] Rubens, Berliner Ber., page 513 (1913).

[11] Eva von Bahr, Verh. d. Deutsch. Ges. **15,** pp. 731, 1150 (1913).

[12] Czerny, Zeits. f. Physik **34,** 227 (Sept. 28, 1925).

[13] Bjerrum, Verh. d. Deutsch. Ges. **16,** 737 (1914).

[14] Sleator, Astrophys. J. **48,** 124 (1918).

[15] Imes, Astrophys. J. **50,** 251 (1919).

[16] Spence, J.O.S.A. and R.S.I. **10,** 127 (1925).

[17] Cooley, Astrophys. J. **52,** 73 (1925).

The frequencies of the centers of bands of this type are determined by the discrete modes of vibration of the molecule, and at least in the case of diatomic molecules these bands should appear in series whose members have approximately equal frequency spacings. This has been found to be the case, although but few bands have ever been found for any one gas. Such bands are not exactly equally spaced, but rather have their frequencies expressed by the formula,

$$\nu_n = n\nu_0(1-nx), \qquad (1)$$

where ν_0 and x are constants for a given substance and $n=1, 2, 3$, etc. This formula has been developed for such cases by Kratzer[18] on the basis of the non-linearity of the law of force which holds between bonded atoms.

An advance has been made in the case of water vapor by Hettner,[19] who has been able to account for the numerous observed absorption bands on the basis of two frequency series and simple additive combinations of members of these series.

It will be noticed that, unlike the ordinary optical spectral series, series of the above type never converge, although their wave-length differences become relatively small, even between members not far from the beginning of the series.

It would seem that we might expect series, similar to the ones characteristic of gases, in the absorption spectra of liquids and solids, although it might be doubtful whether a high resolving power should reveal any duplicity or fine line structure within the bands. The few multiple relations found by Coblentz in his investigations of organic liquids suggest such series. Schaefer and Thomas[20] have shown that all crystalline sulfates have four characteristic absorption frequencies which form a linear series, and the author[21] has found that calcium sulfate has two additional bands which form the fifth and sixth members of such a series.

A C-H SERIES

In an investigation[8] mentioned above the writer showed that all the organic liquids which he investigated had several absorption bands at approximately the same wave-length values. The average values of these wave-lengths for the thirty-one compounds studied in cells of 11 mm thickness are: 0.913μ, 1.023, 1.171, 1.375 and 1.695. As a continuation[21] of this study, a number of compounds were also examined in cells of approximately ten times this thickness, and in each case two new bands appeared, the mean wave-length values of which are 0.760μ and 0.835μ. Among the various compounds these seven bands vary slightly in position, although in no case is there a variation from the mean greater than three percent. These bands are the most outstanding ones of the spectra, but in many cases they have superposed, or partially superposed, upon them minor bands which tend to shift their maximum absorption points from their true positions. Consequently, in searching for series relations among such bands their mean values should be used.

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[18] Kratzer, Zeits. f. Physik **3,** 289 (1920).

[19] Hettner, Zeits. f. Physik **1,** 351 (1920).

[20] Schaefer and Thomas, Zeits. f. Physik **12,** 330 (1923).

[21] Ellis, J.O.S.A. and R.S.I. **8,** 1 (1924).

It was shown that the corresponding frequency values of these bands could be quite accurately expressed as a non-linear series by means of formula (1), which had been developed for gases by Kratzer from theoretical considerations. The values of n in this instance vary from 4 to 10 inclusively. The constants, ν_0 and $\nu_0 x$, were calculated for seven substances. Since this formula was developed upon the assumption that the absorption was due primarily to the oscillations of a pair of atoms, constituting the diatomic gas molecule, it is natural to assume in the case of liquids that the absorption originates from oscillations of a linked pair of atoms within the rather complex molecule. The only type of such a linkage in common to all the substances investigated was a C-H bond, and the above series was attributed to this pair, and may be called a carbon-hydrogen, or C-H series.

Formula (1) may be expressed in terms of two constants, A and B,

$$\nu_n = An - Bn^2, \tag{2}$$

which is a special form of the general parabolic formula which characterizes many phases of band spectra. A and B have been calculated from the average observed frequencies of all the bands observed in the investigation mentioned above, and have the following values:

$$A = 47.37 \times 10^{12}$$
$$B = 0.783 \times 10^{12}$$

The accuracy with which the formula,

$$\nu_n \times 10^{-12} = 47.37n - 0.783n^2 \tag{3}$$

expresses the observed frequencies is shown in Table I.

Extrapolation of formula (3) to include $n=3$, 2 and 1 indicates that bands should be found at 2.22μ, 3.28μ and 6.44μ. The last two lie within the region which must be examined with rock salt spectroscopes, and the writer has already pointed out that bands appearing near 3.4μ

TABLE I

Calculated and observed (average) bands of a C-H series.

n	$\nu\times10^{-12}$ (calc.)	$\nu\times10^{-12}$ (obs.)	λ(calc.)	λ(obs.)
10	395.4	394.8	0.758μ	0.760μ
9	363.0	361.5	0.827	0.835
8	328.8	328.8	0.913	0.913
7	293.4	292.8	1.022	1.023
6	255.9	256.0	1.172	1.171
5	217.5	218.1	1.379	1.375
4	177.0	177.0	1.695	1.695
3	135.2		2.22	
2	91.6		3.28	
1	46.6		6.44	

and 6.8μ in Coblentz's curves are probably to be identified as these bands. Bands near 2.22μ have usually appeared in most investigations, but the writer has shown in the present study that there are several bands in this region, making the exact location of the third member of the C-H series uncertain.

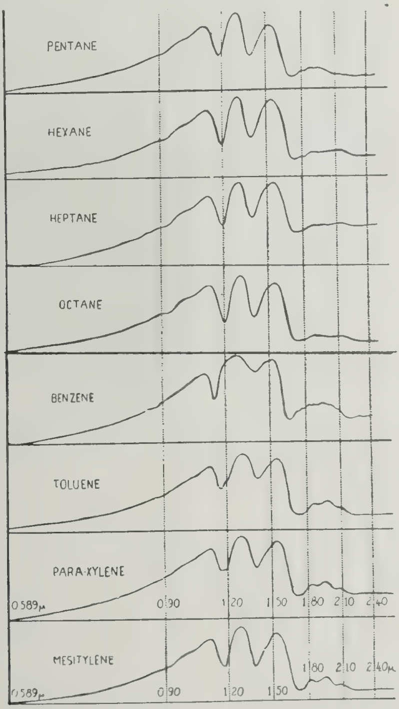

Fig. 1. Absorption spectra to 2.5μ obtained with a registering glass spectrograph. Thickness of cells was 11 mm.

In his recent report Márton[9] also concludes that his observed bands are expressible by an equation similar to (1), and points out that the first member should occur near 6.5μ. He makes no attempt, however, to identify this series with any group within the molecule.

A C-C SERIES

Fig. 1 shows the absorption spectra to 2.5μ, previously published in this journal,[8] of a few relatively simple carbon compounds of both the aromatic and paraffin series. It will be noticed that in addition to the prominent members of the C-H series there are a number of minor bands. These have never been accounted for but an attempt is made in the present work to account for them on the basis of a single-bonded C-C series and simple combinations between this and the C-H series.

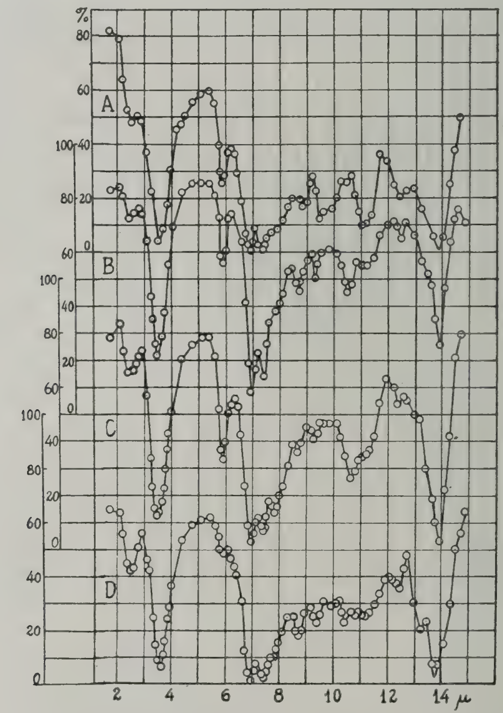

Fig. 2. Spectra obtained by Coblentz with a rock salt spectroscope.
A—0.24mm hexane C—0.15mm dodecane
B—0.15mm octane D—0.15mm hexadecane

Fig. 2 gives a reproduction of some of Coblentz's typical spectra[22] of compounds of the paraffin series, while Fig. 3 gives similar spectra for members of the benzene series. After the bands at 3.4μ and 6.8μ common to these substances, probably the most striking feature is a deep band near 14μ. If we take this as the beginning of a C-C series we meet with only partial success in accounting for the numerous secondary bands of the shorter wave-length region. But if we assume that such a series originates at 28.0μ, a region never investigated for such substances, we can account for these bands in a relatively simple manner.

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[22] Published by permission of the Carnegie Institution of Washington.

Such a series would predict a number of bands in the region between 2μ and 3μ. To search for these, and others, a new self-registering spectrothermograph, recently described by the author,[23] has been assembled. This is equipped with quartz prisms, the combined refracting angles of which are equivalent to 180°. This instrument, although the prisms are small, has a fairly high dispersion.

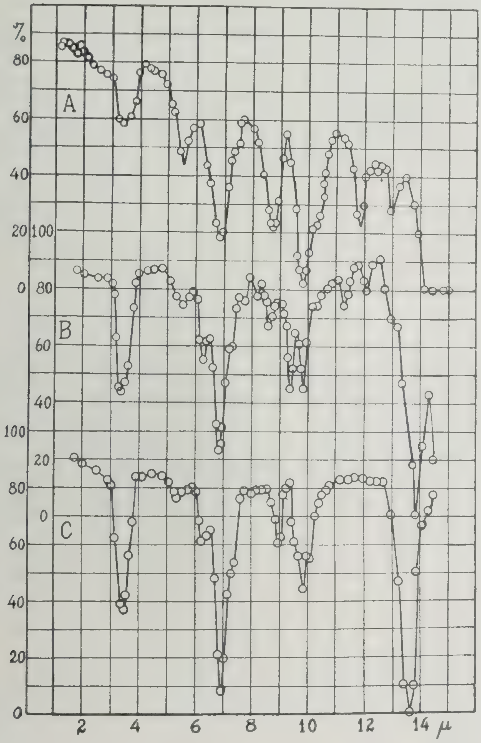

Fig. 3. Spectra obtained by Coblentz with a rock salt spectroscope.
A—0.16mm benzene
B—0.01mm toluene
C—0.01mm o-xylene

Figs. 4 and 5 show the spectra of several compounds obtained for the region between 2μ and 3μ with this machine. The dotted tracing above the absorption curve of p-xylene is an approximation of the original distribution of energy. The atmospheric carbon dioxide band at 2.73μ and the water vapor band at 2.66μ always appear in such a distribution curve.[24]

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[23] Ellis, J.O.S.A. and R.S.I. **11**, (December 1925).

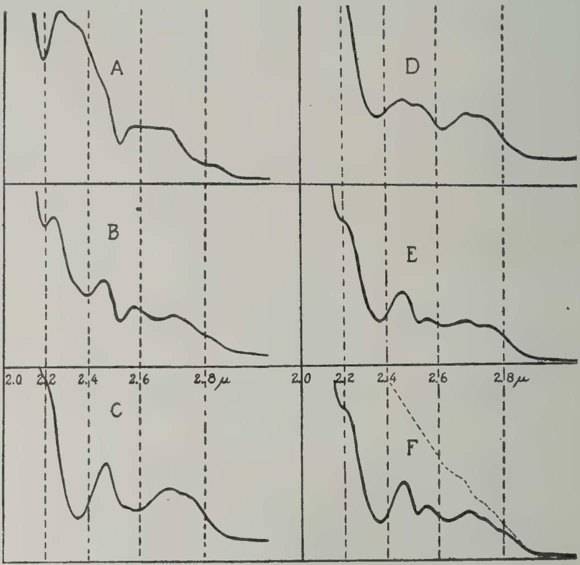

Fig. 4. Absorption spectra obtained with a registering quartz spectrograph.
A—0.05mm benzene D—0.05mm o-xylene
B—0.05mm toluene E—0.05mm m-xylene
C—0.05mm mesitylene F—0.05mm p-xylene

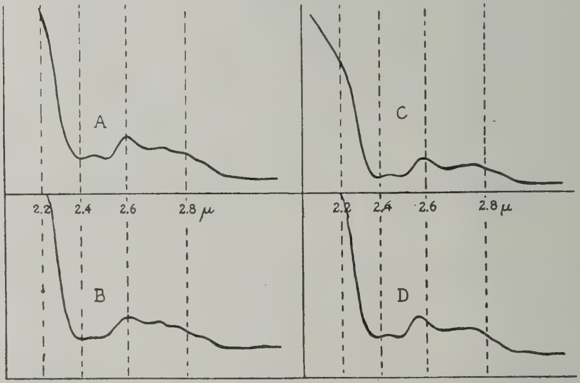

Fig. 5. Absorption spectra obtained with a registering quartz spectrograph.
A—0.05mm pentane C—0.05mm octane
B—0.05mm hexane D—0.05mm decane

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[24] Ellis, Phys. Rev. **26,** 469 (1925).

This method of recording spectra has the disadvantage of not always indicating the relative intensities among the various bands. When the energy curve has a steep slope, a band of considerable intensity may be manifest only by a point of inflection in the absorption curve. Nevertheless, repeated records show that great reliance may be placed upon the details of such curves. Thus, numerous minor bands, of importance in identifying members of a series, especially in the region between 2μ and 3μ have been revealed. As an example, there is no doubt in the writer's mind but the two points of inflection in the spectrum of benzene occurring in Fig. 4 between 2.18μ and 2.52μ represent bands at approximately 2.32μ and 2.44μ. In toluene these have merged together into a broad band with maximum absorption at 2.38μ, yet the duplicity of this band is still apparent. In the higher homologues, the xylenes and mesitylene, this combination band has been so deepened as to partially include the one at 2.18μ.

If we assume a linear series of bands expressible by the formula,

$$\nu_n' \times 10^{-12} = An = 10.71n, \tag{4}$$

or

$$\lambda_n' = 28/n \tag{4'}$$

we seem to be able to trace the series to include about twenty-eight members, in the spectra of compounds of both the chain and the ring type. There are, however, numerous cases in which the bands become partially, or wholly, superposed upon members of the C-H series. In many cases, as heretofore explained, these are manifested by distinct points of inflection; while in other cases, although not capable of detection, these help to account for the abnormal depth of the C-H

TABLE II

Agreement between calculated wave-lengths of the C-H series and corresponding values observed in the spectra of various compounds.

	Calc. λ	benzene C_6H_6	toluene $C_6H_5CH_3$	p-xylene $C_6H_4(CH_3)_2$	mesitylene $C_6H_3(CH_3)_3$	pentane C_5H_{12}	hexane C_6H_{14}	heptane C_7H_{16}	octane C_8H_{18}
λ_1	6.44μ	6.8μ	6.85μ	6.85μ	6.85μ	†	6.86μ	†	6.87μ
λ_2	3.28	3.25	3.45	3.45	3.45	†	3.43	†	3.43
λ_3	2.22	2.18*	2.19*	2.20**	2.20**	**	**		**
λ_4	1.695	1.66*	1.70*	1.705*	1.70*	1.705*	1.72*	1.72*	1.72*
λ_5	1.38	1.39*	1.375*	1.38*	1.37*	1.375*	1.38*	1.38*	1.385*
λ_6	1.172	1.145*	1.155*	1.155	1.18*	1.185*	1.195*	1.19*	1.195*
λ_7	1.022	1.03*	1.025*	1.02*	1.015*	1.015*	1.03*	1.035*	1.035*
λ_8	0.912	0.885	0.915	0.915*	0.915	0.915	0.925	0.925	0.930
λ_9	0.826	†	†	†	0.825	†	†	0.835	†
λ_{10}	0.758	†	†	†	0.750	†	†	0.765	†

* Has another band superposed upon it.
** Occurs as a point of inflection only.
† No measurements recorded.

band. A good example of the latter occurs near 1.18μ, in which region the twenty-third, twenty-fourth and twenty-fifth members of the series of formula (4) become superposed upon the sixth member of the C-H series. It has also been stated that such superpositions cause an apparent shift of members of the C-H series to slightly different wave-length positions; but there are doubtless real shifts in the positions of these bands as well. However, the molecule as a whole has a surprisingly small effect upon these spectra. The agreement of the observed wave-length values of the C-H bands of a number of substances of the two types mentioned above with the values calculated from formula (1) is shown in Table II.

Table III shows the agreement between the observed bands attributed to a C-C series in the spectra of benzene and its simple methyl derivatives and their corresponding members calculated from formula (4). Table IV gives a similar agreement in the case of liquids of the paraffin series.

TABLE III

Calculated and observed wave-lengths in a C-C series for benzene and its homologues.

	Calc. $\nu' \times 10^{12}$	Calc. λ	ben-zene C_6H_6	tol-uene $C_6H_5(CH_3)$	o-xy-lene $C_6H_4(CH_3)_2$	m-xy-lene $C_6H_4(CH_3)_2$	p-xy-lene $C_6H_4(CH_3)_2$	mesity-lene $C_6H_3(CH_3)_3$
λ'_1	10.7	28.0μ	##	##	##	##	##	##
λ'_2	21.4	14.0	14.1μ	13.85μ	13.55μ	12.95μ	12.55μ	11.95μ
λ'_3	32.1	9.35	*	9.3		9.2	9.0, 9.6	9.65
λ'_4	42.8	7.00	**	7.3**	7.3**	7.3**	7.3**	7.3**
λ'_5	53.5	5.60	5.5	5.5	5.35	5.35	5.4	5.5
λ'_6	64.2	4.67						
λ'_7	74.9	4.00						
λ'_8	85.6	3.50	*	*	*	*	*	*
λ'_9	96.3	3.11	*	*	*	*	*	*
λ'_{10}	107.1	2.80	2.8	2.8	2.82		2.78	2.8
λ'_{11}	117.8	2.545	2.52	2.53	2.54	2.52	2.52	2.54
λ'_{12}	128.5	2.33	2.32	2.32**	2.33**	2.33**	2.33**	2.33**
λ'_{13}	139.2	2.15	2.18*	2.19*	2.20*	2.20*	2.20**	2.20**
λ'_{14}	149.9	2.00	2.05*	2.03*	2.0*	2.0*	2.03*	2.02*
λ'_{15}	160.6	1.865	1.855	1.86	1.86	1.86	1.86	1.86
λ'_{16}	171.3	1.75	1.74	1.70*	1.75**	1.75**	1.75	1.75
λ'_{17}	182.0	1.645	1.66*	1.70*	1.64**	1.64**	1.705*	1.70*
λ'_{18}	192.7	1.555			**	**		
λ'_{19}	203.4	1.475	1.47	1.475**	1.46**	1.46**	1.47**	1.47**
λ'_{20}	214.0	1.400	1.39*	1.375*	1.40**	1.40**	1.38*	1.37*
λ'_{21}	224.8	1.335	1.33*	1.375*	1.33**	1.33**	1.38*	1.37*
λ'_{22}	235.6	1.270						
λ'_{23}	246.3	1.215	**	**	1.21**	1.21**	1.195	1.18*
λ'_{24}	257.0	1.165	1.145*	1.155*	1.17**	1.17**	1.155*	1.18*
λ'_{25}	267.8	1.120	1.145*	1.155*	1.11**	1.11**	1.155*	1.18*
λ'_{26}	278.5	1.075			1.06**	1.06**		
λ'_{27}	289.3	1.035	1.03*	1.025*	1.03**	1.03**	1.02*	1.015*
λ'_{28}	300.0	1.000	1.03*	1.025*	1.0	1.0	1.02*	1.015*

* Superposed upon another band.
** Occurs as a point of inflection only.
## Region never investigated.

In these tables the values for the second, third, fourth and fifth members are taken from Coblentz's data, the values for the tenth to the thirteenth members inclusive from the records of the present investigation, while those for the last fifteen members, with the exception of ortho- and meta-xylene and decane, are taken from the writer's curves previously published. The short wave-length values for ortho-and meta-xylene and decane are taken from the new curves of this investigation recorded in Fig. 6.

TABLE IV

Calculated and observed wave-lengths in a C-C series for paraffin compounds.

	Calc. $\nu' \times 10^{-12}$	Calc. λ	pentane C_5H_{12}	hexane C_6H_{14}	heptane C_7H_{16}	octane C_8H_{18}	decane $C_{10}H_{22}$
λ'_1	10.7	28.0μ	††	††	††	††	††
λ'_2	21.4	14.0	†	13.9	†	13.83	†
λ'_3	32.1	9.35	†	9.4	†	9.3	†
λ'_4	42.8	7.00	†	7.35	†	7.35	†
λ'_5	53.5	5.60	†	5.8	†	5.75	†
λ'_6	64.2	4.67	†		†		†
λ'_7	74.9	4.00	†		†		†
λ'_8	85.6	3.50	†	*	†	*	†
λ'_9	96.3	3.11	†	*	†	*	†
λ'_{10}	107.1	2.80	2.8	2.8	†	2.8	2.8
λ'_{11}	117.8	2.545	2.5*	2.5*	†	2.5*	2.5*
λ'_{12}	128.5	2.33	2.33**	2.33**	†	2.33**	2.33**
λ'_{13}	139.2	2.15	**	**	†	**	**
λ'_{14}	149.9	2.00	2.02	2.02	2.0	2.0	2.0*
λ'_{15}	160.6	1.865	1.83	1.83	1.83	1.83	1.90*
λ'_{16}	171.3	1.75	1.75*	1.75*	1.75*	1.75*	1.73*
λ'_{17}	182.0	1.645	1.705*	1.72*	1.72*	1.72*	1.64**
λ'_{18}	192.7	1.555					**
λ'_{19}	203.4	1.475	**	**	**	**	1.47**
λ'_{20}	214.0	1.400	1.38*	1.38*	1.38*	1.385*	1.40**
λ'_{21}	224.8	1.335	1.38*	1.38*	1.38*	1.385*	1.34**
λ'_{22}	235.6	1.270					
λ'_{23}	246.3	1.215	1.195*	1.195*	1.19*	1.195*	1.18*
λ'_{24}	257.0	1.165	1.195*	1.195*	1.19*	1.195*	1.18*
λ'_{25}	267.8	1.120	1.195*	1.195*	1.19*	1.195*	1.18*
λ'_{26}	278.5	1.075					1.08
λ'_{27}	289.3	1.035	1.015*	1.035*	1.035*	1.035*	1.03*
λ'_{28}	300.0	1.000	1.015*	1.035*	1.035*	1.035*	1.0

*	Superposed upon another band.
**	Occurs as a point of inflection only.
†	No measurements recorded.
††	Region never investigated.

It has been pointed out that extrapolation of the C-H series indicates that the first member should occur at 6.44μ. The mean value actually observed by Coblentz for these compounds is about 6.85μ, giving a discrepancy of about +0.4μ. There is a discrepancy of +0.3μ between the observed and calculated values for the fourth member of the C-C series at 7μ. Furthermore, in the case of the open chain compounds there seems to be a corresponding error of about 0.2μ in the fifth member at 5.8μ. These errors, if real, indicate a progressive error in the positions of bands between 3μ and 8μ which reaches a maximum value between 6μ and 7μ and which disappears beyond 9μ. If this error exists, it is doubtless due to inaccurate values of the refractive indices of rock-salt rather than to experimental errors, since measurements by various investigators are fairly consistent in this region. The writer is cognizant of the fact, however, that these indices have been determined by investigators skillful in the technique of infra-red spectroscopy.

There seems to be no detectable deviation from linearity in the case of this latter series, although according to Kratzer the members of the series originate from a cause which should also cause them to depart from a true multiple relationship, namely, the non-harmonic motion of the bonded atoms arising from the non-linearity in the law of force acting. However, in the case of the C-C pair we have a symmetry which is lacking in the C-H group. There probably is a greater amplitude of vibration in the latter case because of the relative lightness of the hydrogen atom, and hence we should expect a greater departure from true harmonic motion than occurs in the oscillations of a C-C pair.

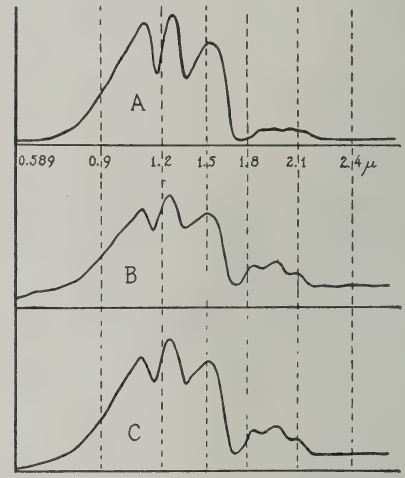

Fig. 6. Absorption spectra obtained with a registering quartz spectrograph.
A—8mm decane
B—8mm o-xylene
C—8mm m-xylene

Combination Frequencies

Kratzer's theory is built upon a quantum theory basis, the absorption frequencies arising from successive integral changes in the rates of

TABLE V

Combination bands of C-H and C-C series.

	calc. $\nu \times 10^{-12}$	calc. λ	benzene	toluene	o-xylene	m-xylene	p-xylene
$\nu_1+\nu'_1$	57.2	5.23	**	5.2	5.35*	5.35*	5.35*
$\nu_1+\nu'_2$	68.2	4.40	4.4				
$\nu_1+\nu'_3$	78.7	3.81	*	*	*	*	*
$\nu_1+\nu'_4$	89.5	3.35	*	*	*	*	*
$\nu_1+\nu'_5$	100.0	3.00	*	*	*	*	*
$\nu_1+\nu'_6$	110.5	2.71	2.75	2.72	2.72	2.72	2.72
$\nu_1+\nu'_7$	122.0	2.46	2.44*	2.38*	2.37*	2.37*	2.37*
$\nu_1+\nu'_8$	132.0	2.27	2.18*	2.19*	2.20*	2.20*	2.20*
$\nu_2+\nu'_1$	102.5	2.93					
$\nu_2+\nu'_2$	113.0	2.65		2.66	2.63	2.63	2.63
$\nu_2+\nu'_3$	124.0	2.42	2.44*	2.38*	2.37*	2.37*	2.37*
$\nu_2+\nu'_4$	134.5	2.23	2.18*	2.19*	2.20*	2.20*	2.20*
$\nu_2+\nu'_5$	145.0	2.07	2.05*	2.03*	2.05*	2.05	2.03*
$\nu_2+\nu'_6$	156.0	1.925	1.89	1.86*	1.86*	1.86*	1.86*
$\nu_3+\nu'_1$	145.5	2.06	2.05*	2.03*	2.05*	2.05*	2.03*
$\nu_3+\nu'_2$	156.5	1.915	1.89*	1.86*	1.86*	1.86*	1.86*
$\nu_3+\nu'_3$	167.0	1.795	1.79*	1.70**	1.86*	1.86*	1.70*
$\nu_3+\nu'_4$	178.0	1.685	1.66*	1.70*	1.70*	1.70*	1.70*
$\nu_3+\nu'_5$	188.5	1.59	1.66*	1.70*	1.70*	1.70*	1.70*
$\nu_4+\nu'_1$	187.5	1.60	1.66*	1.70*	1.70*	1.70*	1.70*
$\nu_4+\nu'_2$	198.5	1.51					
$\nu_4+\nu'_3$	209.0	1.435	1.39*	1.375*	**	**	1.38*
$\nu_4+\nu'_4$	219.5	1.365	1.39*	1.375*	1.36*	1.36*	1.38*

Combination bands of C-H and C-C series.

	calc. $\nu \times 10^{-12}$	calc. λ	mesitylene	pentane	hexane	octane	decane
$\nu_1+\nu'_1$	57.2	5.23	5.35*	#			#
$\nu_1+\nu'_2$	68.2	4.40	**	#	**		#
$\nu_1+\nu'_3$	78.7	3.81	*	#	*	*	#
$\nu_1+\nu'_4$	89.5	3.35	*	#	*	*	#
$\nu_1+\nu'_5$	100.0	3.00	*	#	*	*	#
$\nu_1+\nu'_6$	110.5	2.71	2.72	2.72	2.72	2.72	2.72
$\nu_1+\nu'_7$	122.0	2.46	2.36*	2.38*	2.38*	2.38*	2.38*
$\nu_1+\nu'_8$	132.0	2.27	2.20*	2.38*	2.38*	2.38*	2.38*
$\nu_2+\nu'_1$	102.5	2.93					
$\nu_2+\nu'_2$	113.0	2.65	2.63	2.65	2.65	2.65	2.65
$\nu_2+\nu'_3$	124.0	2.42	2.36*	2.38*	2.38*	2.38*	2.38*
$\nu_2+\nu'_4$	134.5	2.23	2.20*	2.38*	2.38*	2.38*	2.38*
$\nu_2+\nu'_5$	145.0	2.07	2.02*	2.0*	2.0*	2.0*	2.08*
$\nu_2+\nu'_6$	156.0	1.925	1.86*	1.9*	1.9*	1.9*	1.90*
$\nu_3+\nu'_1$	145.5	2.06	2.02*	2.0*	2.0*	2.0*	2.08*
$\nu_3+\nu'_2$	156.5	1.915	1.86*	1.9*	1.9*	1.9*	1.90*
$\nu_3+\nu'_3$	167.0	1.795	1.70*	1.75*	1.75*	1.75*	1.80
$\nu_3+\nu'_4$	178.0	1.685	1.70*	1.705*	1.72*	1.72*	1.72*
$\nu_3+\nu'_5$	188.5	1.59	1.70*	1.60*	1.72*	1.72*	**
$\nu_4+\nu'_1$	187.5	1.60	1.70*	1.60*	1.72*	1.72*	**
$\nu_4+\nu'_2$	198.5	1.51					
$\nu_4+\nu'_3$	209.0	1.435	1.37*	1.375*	1.38*	1.385*	**
$\nu_4+\nu'_4$	219.5	1.365	1.37*	1.375*	1.38*	1.38*	1.37*

* Superposed upon another band.
** Occurs as a point of inflection only.
# No measurements recorded.

vibration within the molecule. It would seem probable that if a carbon atom is bonded both to a hydrogen and another carbon atom that a new frequency ν_c would be absorbed provided that

$$\nu_c = \nu_m + \nu_n' \qquad (5)$$

where ν_m and ν_n' are low frequency members of the C-H and C-C series respectively. This means that a quantum of energy would be divided between the two absorbing centers.

Table V shows the new absorption frequencies to which such a phenomenon would give rise, and an attempted identification of their corresponding wave-lengths with bands actually observed in the curves of Figs. 1-6. The two series, with these simple combinations, seem to satisfactorily account for practically all of the bands, up to about 7μ, observed in the spectra of the simple hydrocarbons. In no case do these series demand a band of major intensity which cannot be accounted for. The bands predicted by formulae (4) and (5) between 3.5μ and 5.5μ do not appear in the ordinary spectra, probably because of the unusually low dispersion of rock salt in this region and the thinness of absorption cell used. In the instances where Coblentz used a large spectrometer, of greater resolution, many of these bands appeared. Their values have been included in Tables III, IV and V. The numerous bands occurring more or less regularly between 8μ and 15μ, for all substances, and the rather prominent band at 6.2μ in the spectrum of benzene and its derivatives, are not accounted for by such series.

It also seems that the conditions would be appropriate for a division of an energy quantum between two C-H groups sharing the same carbon atom. This would cause the second member of the C-H series to appear with unusual intensity. This phenomenon is observed, especially in the spectra of the paraffin compounds, as may be seen in Fig. 2.

Methane, CH_4, should have a very simple spectrum, since it has only bonds of the C-H type. Coblentz's curve shows it to have but three absorption bands, at 7.7μ, 3.31μ and 2.35, which may be identified as the first three members of the C-H series, in spite of the shift of the first member toward longer wave-lengths. In the spectrum of ethane, C_2H_6, these three bands appear, with the first member in the position which it occupies in the spectra of the higher liquid members of the paraffin series to which this gas belongs. It is impossible to identify any members of a C-C series, although there is an undefined group of bands at 12μ. In the spectrum of butane, C_4H_{10}, we have the three C-H bands as in ethane, and in addition there are bands at 14μ and

5.65μ which may be identified as the second and fifth members respectively of a C-C series.

In the spectra of the ring compounds there is a considerable variation in the position of the 14μ band. This band shifts progressively toward a shorter wave-length value with successive substitutions of a methyl group, CH_3. In the spectra of the xylenes, $C_6H_4 \cdot (CH_3)_2$, the position of this band also depends upon the positions of such substituted groups. Table VI shows the displacements of this band. Its average value for all the compounds examined by Coblentz is about 13.7μ. The shorter wave-length spectra of the compounds of Table VI are quite similar.

TABLE VI

Displacement of the 14 μ band in the spectra of the benzene derivatives.

benzene	14.1μ
toluene	13.85
o-xylene	13.55
m-xylene	12.95
p-xylene	12.55
mesitylene	11.95

If C-C and C-H pairs of atoms give rise to linear, or approximately linear, series of absorption bands, then we should expect other bonded pairs within the molecule to behave in a similar manner. In a later paper it will be shown that the shorter wave-length bands occurring in addition to the members of the C-H series in the spectra of simple halogen derivatives of the benzene and paraffin series can be accounted for on the basis of carbon-halogen series starting near 17μ, and combinations between such series and the carbon-hydrogen series.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF CALIFORNIA, SOUTHERN BRANCH,
November 30, 1925.

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CHANGES IN THE REFRACTIVE INDEX OF HELIUM PRODUCED BY A GLOW DISCHARGE

By W. H. McCurdy* and A. Bramley

Abstract

Interferometer method of measuring the concentration of ions and excited atoms in a glow discharge.—According to the Lorentz theory, the presence of atoms in a state *s* should change the index of refraction of the discharge for light of wave-length $(\lambda=\lambda_s+\delta\lambda_s)$ by an amount $\delta n=(N_s e^2/8\pi^2c^2m)(\lambda^3_s/\delta\lambda_s)$, where N_s is the concentration of excited atoms. Kramer's theory leads to a somewhat different relation. To measure δn, a Michelson interferometer was used into one arm of which was introduced a cylindrical discharge tube with a filament cathode in a side arm, and a ring anode, so that the light passed along the positive column. In the tests made with He, an iron arc was used as source, and the light from the half silvered mirror was focussed on the slit of a spectrograph. When the glow discharge was started (30 to 40 m-amp.), shifts to .2 to .5 fringe were observed for about 15 Fe lines. In each case the shift was positive or negative according as the wave-length was greater or less than that of a neighboring He line. The results are not quantitative as yet but prove the practicability of the method.

PREVIOUS methods of determining the concentration of ions in gaseous discharges[1] may introduce electrical disturbances arising from the presence of exploring electrodes which, in some cases, cause doubt about the accuracy of the results. Furthermore, these methods are powerless to detect or to measure the concentration of excited atoms or molecules, which often play an important rôle.[2] For these reasons the following optical method has been devised to measure these concentrations and the preliminary tests prove it to be capable of practical application. The method is based on measurement of the refractivity of the gas in the spectral region close to emission or absorption lines in its spectrum, and the interpretation of these measurements by current theories of optical dispersion. The possibility of making such measurements was demonstrated by Ladenburg and Loria.[3]

The apparatus (Fig. 1) consisted of a discharge tube 6 inches (15.2 cm) long, placed in one arm of a Michelson interferometer. The tube itself was made with a hot cathode *F* in a side tube and a ring anode *A* through which the light could pass, and with the two optical glass end plates cemented to the ground ends of the tube. By this arrangement the part of the discharge in the arm of the interferometer included only the positive column, which contains the highest concentration of excited atoms.

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* National Research Fellow in Physics.

[1] Langmuir and Mott-Smith, Gen. Elec. Rev. **26**, p. 731 (1923); **27**, pp. 444-538 (1924).

[2] Compton, Turner and McCurdy, Phys. Rev. **24**, p. 597 (1924).

[3] Ladenburg and Loria, Verh. d. D. Phys. Ges. **10**, p. 858 (1908).

The success of the experiment depended upon the use of light of practically the same wave-length as that of a line in the spectrum of the positive column. A strong iron arc *S* was used as the source of light for the interferometer. The light, after passing through the interferometer, was bent to a convenient direction by a right angle prism *P* and focussed by a system of lenses on the slit *I* of a monochromatic illuminator of good resolving power. The fringes were then observed by means of a telescope after the light had been resolved by the illuminator. In order to measure the amount of shifting of the fringe system on starting or stoping the discharge, the telescope was replaced by a camera with an equivalent lens system. The displacement of the fringe system due to the change in refractive index on starting the discharge, was recorded with the camera by taking three adjacent exposures, the two outside being with no discharge while the center one was taken with the discharge running. This gave a convenient method of determining the fraction part of a fringe separation by which the system had been moved by the action of the discharge.

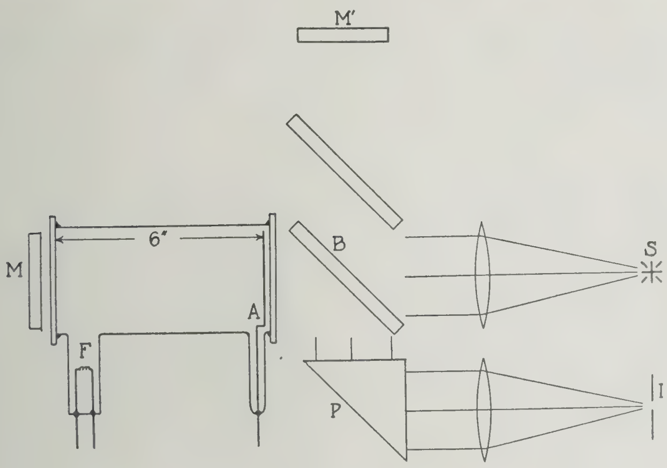

Fig. 1. Diagram of apparatus.

As this method depends on measuring the change in the refractive index of the gas with regard to a certain line when the discharge is started, we will next consider the various formulas which connect the index of refraction with the concentration of atoms in the various states. According to Lorentz's formula, the index of refraction n is connected with the wave-length λ of the light used and concentration N and natural wave-length λ_s of the atoms in the s state by the relation

$$n^2-1=\frac{e^2}{4\pi^2c^2m}\,\frac{N_s\lambda_s^4}{(\lambda^2-\lambda_s^2)}+\text{const.},\tag{1}$$

if λ_s differs from λ by a small quantity. Taking the case of normal incidence of light on the mirrors, the condition for a fringe (darkness) at a given position is

$$2dn=p\lambda$$

where p is an integer and d is the difference of the distances of the two mirrors M and M' from the half-silvered mirror B. Thus the change in n corresponding to a fractional shift f is

$$\delta n=(\lambda/2l)f\tag{2}$$

where l is the length of the tube. Letting $\lambda=\lambda_s+\delta\lambda_s$ we find for N_s in terms of f, λ_s and $\delta\lambda_s$ the expression

$$\mathrm{N}_s=\frac{4\pi^2c^2m}{e^2l}\,\frac{\delta\lambda_s}{\lambda_s}\qquad=10\frac{\delta\lambda_s}{\lambda_s^2}f\tag{3}$$

where $\delta\lambda_s$ is measured in angstroms and λ_s in microns.

According to Kramers,[4] if the atom is in a state s which absorbs energy of frequency $\overset{a}{\nu}_{s_1}\cdots\overset{a}{\nu}_{s_n}$ and emits energy of frequency $\overset{e}{\nu}_{s_1}\cdots\overset{e}{\nu}_{s_n}$ under the influence of external radiation, while $\overset{a}{A}_{s_1}\cdots\overset{a}{A}_{s_n}$ and $\overset{e}{A}_{s_1}\cdots\overset{e}{A}_{s_n}$ represent the probabilities of a transition from the state s to a lower or higher energy level with the emission or absorption of energy respectively, and if N is the total number of atoms and $\overset{a}{\tau}_{s_i}$ and $\overset{e}{\tau}_{s_i}$ represent the life of the excited state s_i for the frequency $\overset{a}{\nu}_{s_i}$ and $\overset{e}{\nu}_{s_i}$, then

$$n^2-1=N\left[A_s^a\tau_s^a\frac{e^2}{4\pi^2c^2m}\,\frac{(\lambda_s^a)^4}{(\lambda^2-(\lambda_s^a)^2)}-A_s^e\tau_s^e\frac{e^2}{4\pi^2c^2m}\,\frac{(\lambda_s^e)^4}{(\lambda^2-(\lambda_s^e)^2)}\right]+\text{const.},$$

where λ_s^a and λ_s^e lie near λ. Since the above type of apparatus measures only the change in refractive index in the neighborhood of a particular line, the frequency λ_s^a must equal λ_s^e and Kramer's equation becomes

[4] Kramers, Nature, May 10, 1924, p. 273 and Aug. 30, 1924, p. 310.

$$n^2-1=\frac{e^2N}{4\pi^2c^2m}\left[A_s^a\tau_s^a-A_s^e\tau_s^e\right]\frac{\lambda_s^4}{(\lambda^2-\lambda_s^2)}+\text{ const.}$$

The quantity $N[A_s^a\tau_s^a-A_s^e\tau_s^e]$ which replaces the concentration N_s of Lorentz's classical formula, represents the average increase per unit time in the number of atoms in the state s due to the absorption and emission of light of frequency ν_s.

In the following table are given the observed fringe shifts for the various excited states of He, investigated in the visible and violet region of the spectrum by this method. The intensity of the lines are given in the bracket, while the shifts are given as fractions of one fringe spacing. In addition to these, shifts with about eight other lines were observed visually, but not measured. In all cases the shift was positive or negative, according as the light was of wave-length greater or less than that of the neighboring helium line. As no shift could be observed for the lines which were 30 or 40 Angstroms from the nearest line of the helium spectrum, the temperature change on starting the discharge must have been negligible.

TABLE 1

Current in tube	State	He line	Fe line	Shift
30 m-amp	$1P-3D$	4921.929 (4)	4920.52 (6)	−.4 fringe
30	$1P-4D$	4387.928 (3)	4383.55 (10)	−.3
40	$1P-4D$	4387.928 (3)	4404.	.18*
40	$1P-5D$	4143.77 (2)	4143.88 (6) 4143.43 (6)	−.5†
35	$1P-2S$	5047.736 (2)	5049.8 (5)	−.12

These results prove the practicability of the method and the possibility, with refinements and added data, of testing the existence of negative terms postulated in Kramer's dispersion formula and of using refractivity to measure the distribution of atoms in excited states in a discharge. This further work is now being carried on by one of us (W. H. Mc.).

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PRINCETON, N. J.
October 14, 1925.

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* This shift appears to be too large. The observed effect is probably in error.

† This shift might have been either + or − in sign as it was impossible to tell from the photographs in which direction the shift had occurred without taking visual observations.

COMPLEX MAGNETIZATION

By Eugene Peterson

Abstract

Magnetization of silicon steel by two sinusoidal fields of differing frequencies.—*The energy loss per cycle W* and the *flux density B* associated with each of the two frequencies were determined when the two sinusoidal magnetizing forces were simultaneously impressed on a toroidal silicon steel core built up of one-mil laminations. A null method was used which permitted suppression of the modulated currents and constancy of the impressed currents during manipulation for balance. The frequencies used were 400, 821 and 1582. Six sets of measurements were taken with fixed magnetizing forces ranging from 0.5 to 10 gilberts/cm and superposed forces up to 15 gilberts/cm. The results show that the effect of superposition depends upon the relative amplitudes and upon the frequency ratio R of the superposed frequency to the other. At low fixed fields W and B go through maxima as the superposed field is increased, the maximum value increasing with R. The maximum is less pronounced or absent for the higher fixed fields. In general B is smaller with a low than with a high value of R other things being equal. The effect on W is not as sharply defined; in general the effect of superposition is more pronounced the higher the superposed frequency. The amplitude effect and frequency ratio effect are shown to be in general agreement with conclusions drawn from mathematical treatment of somewhat simplified cases and it is concluded that the effects are not inconsistent with purely hysteretic phenomena.

THE present investigation is concerned with the behavior of iron under the simultaneous influence of two sinusoidal magnetizing forces, particularly with reference to the distribution of flux and of energy loss between the two superposed frequencies. The problem has apparently received no consideration although numerous investigators have determined the effect of an alternating magnetizing force on the flux due to a constant or slowly varying magnetizing force,[1] and others have determined the flux and energy associated with a high frequency force at various points of a cycle of low frequency magnetization.[2]

Experimental Arrangement

Supression of modulation. The varying reaction of an iron core coil during a cycle of the impressed field gives rise to new frequencies which are the sum and difference of integral multiples of each of the two impressed frequencies such that the sum of the integers is odd. Two distinct effects are produced by the flow of these modulated currents; the problem is complicated in a manner which is unknown since the effect is precisely the one in question in the simplest possible case of two impressed frequencies, and further, the flow of modulated current must produce in general an effective resistance and reactance to the fundamental frequencies. It is certain then that an investigation of the properties of iron under the action of alternating forces must be carried out in the absence of modulated components in the magnetizing force.

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[1] From Lord Rayleigh, Phil. Mag. 1887, to Spooner Phys. Rev. April 1925.

[2] Turner, Phys. Rev. **21,** 74 (1923).
Fondiller and Martin, J.A.I.E.E. 1921.

The desired suppression may be approximated to a satisfactory degree through the use of networks as shown in Fig. 1A marked $f_1 f_2$, which have the properties that energy from the sources is transmitted to the coil with small attenuation, that a high impedance is offered to frequencies outside the transmitted range, and that the surge impedance of the networks is large compared to the coil impedance. This method also permits us to measure each of the two current components by inserting thermocouples and associated micro-ammeters at the points $T_1 T_2$ indicated in the figure.

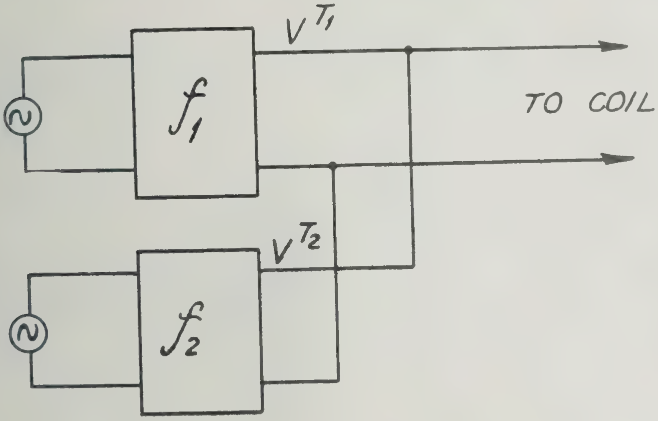

Fig. 1A

Method of measurement, flux density and loss per cycle. The necessity for suppressing modulated components and the convenience of keeping the currents constant during a measurement led to the adoption of two methods,* one involving a Braun tube and the other involving an aural balance. The latter was used for the quantitative determination since it is capable of greater precision than the first; the first, however, enables one to explore the field in qualitative fashion (visually) in a comparatively short time; we may dispose of it with the statement that it depends upon the integration of the voltage due to the flux change by a condenser, and that desired components are selected by tuned circuits, amplified without distortion, and impressed upon the Braun tube plates to give component B-H ellipses.

---

* These conditions rule out the usual type of bridge. Suppression of modulated components may be effected in the bridge by inserting two large inductance coils having a high coupling coefficient in the two branches between which the generator current divides—and in one of which the iron-core coil is placed. The second condition is then unsatisfied however.

The following null-method, which was used for the quantitative determination, is based upon the balancing of two voltages proportional to the flux and to the magnetizing force respectively. The particular arrangement used is shown in Fig. 1B, and involves the variation of capacity C and resistance r to attain balance, the other quantities R_0, r_1, R_φ and C_φ being fairly well fixed.

The two potentials to be balanced are taken from R_0 and C_φ respectively, and phase and amplitude adjustments are effected through r_1, r, and C which are connected in series across R_0. The potential across C_0 is taken from a closely coupled secondary through a relatively high resistance in order that the secondary may have inappreciable reaction upon the primary, as well as to have the measurements independent of the primary winding resistance. R_0 is made small compared to r_1 to keep the primary currents unchanged throughout the manipulation for balance; if it were otherwise the observations at definite currents would involve successive approximations or the equivalent.

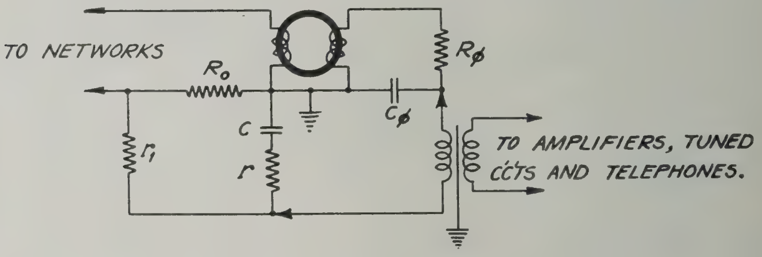

Fig. 1B

A succession of amplifiers and tuned circuits is used to provide a sensitive indication of the balance point in connection with telephone receivers. The first stage of the amplifier is made to have a large load capacity so that modulation may not take place in the amplifier itself, since the balancing of the two voltages refers simply to a single frequency, and the tuned circuits are used to eliminate disturbing components produced by the coil which would otherwise obscure the null point since there are always, in general, modulated components near the fundamentals.

At the null point it may be shown that the flux linking with the secondary is given by

$$B=\frac{C_\varphi R_0 I}{n\sigma}10^8\left(\frac{(R_\varphi^2+1/p^2C^2_\varphi)(r^2+1/p^2C^2)}{(R_0+r+r_1)^2+1/p^2C^2}\right)^{\frac{1}{2}}$$

where n is the number of turns of wire on the secondary, σ is the core cross-section and I is the primary current, and that the phase angle of B referred to H is given by

$$\theta=\cot^{-1} pC(R_0+r+r_1) -\cot^{-1}pCr-\cot^{-1}pC_\varphi R_\varphi.$$

The energy loss in ergs per cycle per cc of core material is given by

$$4W_k=\Sigma B_k H_k \sin\theta_k$$

in which k refers to the component.

Instability of current[3] with applied e.m.f. is avoided by making the ratio of resistance to reactance of the circuit large, as may be shown analytically by application of the method of perturbations[4] to a simple B-H characteristic, and this condition works in the same direction as the condition for the suppression of modulated components.

Connections and apparatus were shielded and spaced inasmuch as high potentials were developed in the networks which would otherwise induce potentials in the sensitive amplifiers used to indicate balance and so lead to a false null-point. Further, shielded transformers were used at appropriate points to reduce capacitive coupling between the two sides of the shield. As a result of these precautions the currents at the highest frequency employed (1582 cycles) were found to be the same within one-third percent (within the error of observation) in the two wires leading to the coil, and the amplifier was found to have no potentials induced when the input terminals were short-circuited.

The frequencies chosen for the work were 400, 821 and 1582 cycles so that there were available frequency ratios of 3.95, 2.05, 1.93 and their reciprocals, made non-integral to avoid effects due to the relative phase of the two inputs, and adjusted to avoid formation of comparatively low impedânce paths to the modulated products* of low order. These frequencies were used in pairs during the experiments and were supplied by vacuum tube oscillators and amplifiers, the frequency and amplitude being quite stable.

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[3] Martienssen, Phys. Zeit., **11**, 448, (1910).

[4] Analogous to Appleton's treatment af the vibration galvanometer. Phil. Mag. **47**, 609 (1924).

*The last effect may be avoided in this case by using the bridge arrangement mentioned in the previous note.

The specimen. The core was built up of 17 rings of one mil (.025 mm) silicon steel having an inside diameter of one-half inch (1.27 cm) and a radial thickness of one-sixteenth inch, the weight being 0.237 gr and the cross-section .0070 cm^2. The winding consisted of two sections of 750 turns each uniformly distributed about the core and arranged to produce no cross-magnetization, by having alternate layers wound with a negative pitch. The coupling coefficient was measured at a low force and found to be 0.99; the turns ratio was found by reversing the windings to be 1.02, so that the data presented are to be increased by one percent. The resonant frequency of the coil under test was found to be of the order of 50,000 cycles so that resonant effects in the windings have negligible effect on the measurements.

EXPERIMENTAL PROCEDURE

Six sets of measurements were taken over the range of magnetizing forces from 0.5 to 10.0 gilberts/cm r.m.s. so as to include regions on both sides of the maximum a.c. permeability which is found at about 2.5 gilberts/cm. The procedure followed during the measurements was to have the output of the oscillator supplying the measured frequency maintained constant so as to give 0.5, 1.4, 2.5, 4.4, 7.0, and 10 gilberts/cm in turn, and with the tuned circuits adjusted, to balance at a number of values of superposed current for each of the six frequency combinations.

In this sort of work the balance point drifts with time and depends upon the previous magnetic history. To make matters definite, therefore, a fairly large magnetizing force was applied for a few minutes before each run and the measurements proceeded from large fields down to small ones. It was usually found possible to check the results at different times to within five percent, although the settings were made usually to three or four places. The precision of adjustment was thus greater than the stability of the iron.

EXPERIMENTAL RESULTS

Flux Density. For clearness in presenting the results we have plotted the flux densities (Fig. 2) and energy losses per cc per cycle (Fig. 3) separately and, of the six constant fields H' at which the amplitude and frequency of the superposed field H were varied, three of the more representative ones have been plotted, corresponding to the fields H' 0.5, 2.5, and 7.0 gilberts/cm. The difference in the six curves plotted for any one value of H' proceeds simply from the different frequency ratios involved. Flux densities and magnetizing forces are specified by r.m.s. values and the energy loss per cc per cycle is given in ergs.[1]

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[1] The ordinates of Figs. 2, 3 are to be multiplied by 1000.

Thus to consider flux densities first we have at $H' = 0.5$ a group of which the topmost curve represents the effect on the B at 400 cycles of a superposed H at 1582 cycles, which for convenience may be designated as the B_4-H_{16} characteristic. B increases by a factor of over four as H_{16} increases to 1.6 and then decreases at a slower rate. The next lower curves representing B_4-H_{16} and B_4-H_8, are almost coincident and reach maxima slightly less than four times the initial flux density. The curves B_8-H_4, B_{16}-H_8, B_{16}-H_4, reach maxima of about 2.5 times the initial and are almost coincident. To sum up, the effect of a superposed force at $H' = 0.5$ is to cause the flux, or, what is the same thing, the permeability to pass through a maximum, the magnitude of the maximum being greater for the lower frequency than for the higher. At large superposed fields all characteristic curves tend to coincide.

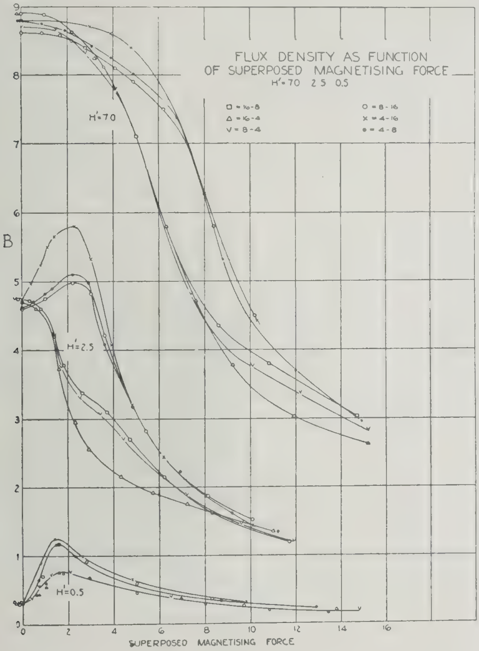

Fig. 2

At an H' of 1.4 (not shown) the curves lie in the order of the frequency ratio. Superposition produces a smaller increase (a ratio of less than two in the case of B_4-H_{16}) than was the case of an H' of 0.5, but the B_{16}-H_4 characteristic diverges more than it did at the lower H and drops decidedly after passing through a slight maximum at a low H. Passing on to the second group for an H' of 2.5 at which the permeability is maximum, we find the increase due to superposition to be twenty-two percent for B_4-H_{16} and about ten percent for B_4-H_8 or B_8-H_{16}. The maxima are found at larger superposed H's than was the case in the previous curves, and it seems that the superposed H required is slightly greater when the ratio of the superposed frequency to the original decreases. When the superposed H is made lower in frequency than the original, the curves pass through no maximum but decrease slowly at first and then rapidly, and seem to approach the H axis asymptotically. The curves again lie in the order of their frequency ratios.

The results obtained with fields of $H'=4.4$, 7.0 and 10, of which only one ($H'=7$) is plotted, are very similar and again the curves are found arranged according to frequency ratio.

We may summarize the effect of superposition upon flux density (or its equivalent in this case; permeability) by saying that with two impressed frequencies the flux of the low frequency is greater than that of the high frequency over the greater part of the characteristic so that the low frequency will pass through higher maxima, or the high frequency will start to decrease at lower superposed fields. There is apparently a further influence of the frequency ratio, such that a greater frequency ratio leads in general to a more pronounced effect and this is evidenced with frequency ratios differing by as little as six percent. This answers the question as to the partition of flux between the two frequencies impressed; the lower frequency has the greater flux density with equal fields of the two frequencies.

Energy Loss per Cycle. The determination of energy loss is somewhat less definite than that of flux since the variation with time appears to be somewhat greater. The results, with the same fields as those used for the flux density measurements, are shown in Fig. 3. The first group at $H'=0.5$ exhibits a larger change (maximum ratio of 6.3, minimum of 3.2) with superposed H than did the flux, and the maxima are found in general at lower superposed H's. As with the flux the group of curves representing the effect of a higher superposed frequency lies above that representing a superposed frequency ratio of less than unity, considering the region near the maxima, but the curves are no longer ordered within each group corresponding to the frequency ratio. There also appears some tendency for the two groups to interchange relative positions at high fields. When the constant magnetizing force is maintained at 1.4 (not shown) the two frequency groups show the same effect but the change in energy loss is much reduced, as was true of the flux in similar circumstances. The curves are ordered according to the frequency ratio in the neighborhood of the maxima although they show a tendency to cross one another at higher fields. At $H'=2.5$ the energy peak is much reduced. The curves for superposed frequency ratio greater than unity pass through more pronounced maxima than the lower frequency ratio group, the two groups intersecting at large fields. The effect of eddy currents is apparent from the order of the curves at zero superposed H, the ordinates increasing with the measured frequency.

At $H'=4.4$ (not shown) we find more pronounced maxima and greater rate of decrease for the higher ratio group. The results for $H'=7$ and for $H'=10$ (not shown) are quite similar bringing out the relations more clearly, and also showing a greater effect of eddy currents. It is only for ratios of superposed to measured frequency greater than unity that a maximum occurs, and these characteristics exhibit the greatest rate of decrease. Except for the effect of eddy currents, for which allowance may be made roughly from the initial values, the curves appear to be ordered as to frequency ratio.

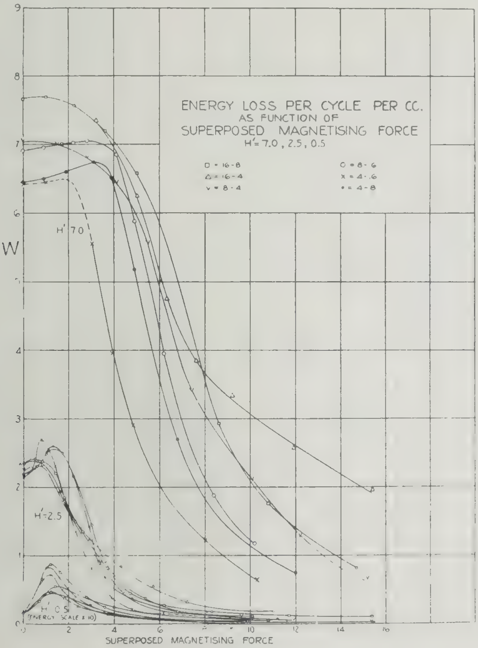

Fig. 3

We may summarize the results of the experiments on energy loss per cycle as follows: The maxima with high superposed frequencies are more pronounced and the decrease is more rapid beyond the maxima so that in general as we pass out to increased superposed fields we find the order of the characteristics inverted; the high superposed frequency curves lie below the lower frequency ones. Thus the partition of energy loss between the two input frequencies depends decidedly upon the superposed field strength. These effects are somewhat masked by eddy current losses at high fields but the same conclusions may be made if we adjust the curves corresponding to the different frequencies to have the same initial energy loss. The maxima are found at all fields investigated when the superposed frequency is greater than that measured. The course of the phenomenon bears a general resemblance to that of flux density although the maxima occur at lower superposed fields.

It is easy to find regions in which the total energy loss under superposed conditions is less than the energy loss with a high frequency alone impressed; this corresponds to hysteresis suppression and appears to find a ready explanation in the shifting of the displaced high frequency loops to regions of small energy loss which exist along the more nearly saturated parts of the magnetization characteristic.

It may be stated that other magnetic materials, permalloy for example, show the same sort of effects due to superposition as those observed in silicon steel.

Discussion of Results

One question which arises upon inspection of the data is as to the cause of the frequency ratio effect there evidenced; a complete answer is of course impossible but it may at least be shown that the frequency ratio effect is not inconsistent with a hysteresis cycle, itself independent of the frequency or frequency ratio. The hysteresis loop used for the analysis is obtained from Honda and Okubo's extension[5] of Ewing's model which presents perhaps the least unsatisfactory picture of the course of the B-H loop. Fig. 4 represents a typical loop in which the equilibrium axis of a single complex is taken at 60° to the axis of the impressed magnetizing force; the full lines represent stable states and the dotted lines unstable states. Subsidiary loops are to be observed. The result is independent of the frequency of the applied force except in so far as temperature agitation may cause irreversible changes through shifting in effect the angle of the complex.

We now suppose a two-frequency magnetizing force to be impressed on a loop idealized by having the lines representing stable states parallel to the h-axis and by putting unstable states at convenient points. The two fundamental components may be calculated by the usual methods of Fourier analysis which are rather long in the cases considered despite the simplifications mentioned above. The results of the calculation are tabulated below:

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[5] Honda and Okubo, Tohoku Univ. Sci. Report **V**, 153 (1916).

Ratio of Measured to Superposed Frequency	Flux Density proportional to	Energy Loss per Cycle proportional to
1:5	9.65	8.25
1:3	8.36	6.15
3:1	6.71	5.94
5:1	4.56	3.99

and are observed to be ordered as to frequency ratio; we may conclude that the frequency-ratio effect is capable of production by purely hysteretic loops.

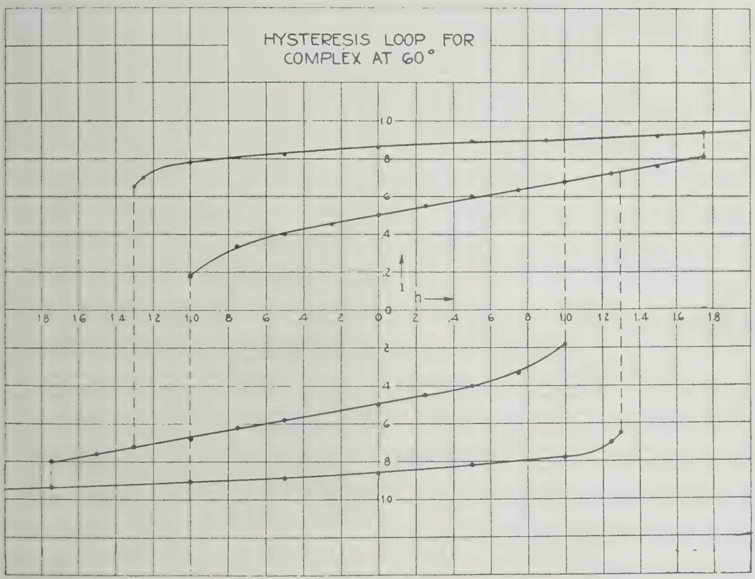

Fig. 4

The curves obtained experimentally in the case of a large ratio of the superposed to the measured frequency are similar to those obtained with a single constant impressed force plotted as a function of temperature in this respect, that the flux passes through a maximum at low fields and decreases progressively at high fields. A complex may possibly take up the increased energy due to heat in two ways; in changing the angle of the lattice considered as a whole—an organizing effect because of the irreversible changes mentioned above—and in changing the angles of the elementary magnets within the complex which would have a disorganizing effect. Apparently the first effect is preponderant with small magnetizing forces and the second necessarily with large forces. The effect of a superposed magnetizing force differs from that of heat since the superposed force is applied substantially along a unique axis at a definite frequency.

It may be shown that in the case of a small high frequency and a large low frequency force, the high frequency permeability depends roughly upon the permeability to the low frequency field and that the low frequency flux is practically unaffected by the superposed high frequency, as is found experimentally. This is accomplished by expressing the hysteresis loop branches of a family of hysteresis loops by double power series and combining in a Fourier series for a complete cycle.

The writer acknowledges his obligation to Professor Wills and to Professor Webb of Columbia University for suggestions and encouragement.

Bell Telephone Laboratories, Incorporated
November 18, 1925.

ASSOCIATION, ADSORPTION, AND DIELECTRIC CONSTANT

By C. T. Zahn

Abstract

Dielectric constant of water vapor at pressures 3 to 20 mm and at temperatures 23 to 165°C.—Using a heterodyne beat method previously described, a study has been made of the variation of the dielectric constant with pressure and temperature. At room temperature, the curve connecting $(\epsilon-1)$ with pressure consists of two straight parts connected by a transition curve. This change of slope is less marked at higher temperatures and disappears at about 47°C. The rectilinear portion below the transition pressure corresponds to the normal behavior of water vapor. The abnormal behavior above the transition pressure cannot be explained satisfactorily by the association theory suggested by Jona in connection with his results. It is suggested, rather, that the anomaly is due to the formation of an adsorbed layer of water on the condenser plates. As the number of adsorbed molecules increases, the vapor pressure increases, approaching the ordinary vapor pressure as a limit. The final thickness of the layer at saturation pressure is of the order of the radius of molecular attraction and comes out of the order of several microns, corresponding to about 200 molecular layers. The experimental results are in general agreement with this theory.

IN a recent series[1] of measurements of the dielectric constants of a number of dipole gases by the author, complete agreement with the Debye theory was obtained except for the possibility of very slight deviations in one or two cases. On the other hand experiments by Jona[2] showed marked anomalous increases of the dielectric constant near the liquefaction points of several vapors. SO_2 among others showed a considerable increase. More recent observations by the author did not show this effect. Jona attributed the effect to association of the molecules with an accompanying increase in the electric moment of the resulting molecule. On account of these apparent inconsistencies a more thorough investigation of this effect has been made both theoretically and experimentally.

Association and the Dielectric Constant

Debye's equation may be put in the form

$$(\epsilon-1)=N(a+b/T)$$

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[1] C. T. Zahn, Phys. Rev. **4,** 400 (1924).
C. P. Smyth and C. T. Zahn, Journ. Amer. Chem. Soc. **47,** 2501 (1925).
And recent data on CO_2, NH_3, and SO_2 about to appear.

[2] M. Jona, Phys. Zeits. **20,** 14 (1919).

where ϵ is the dielectric constant, N the number of molecules per cubic centimeter, T the absolute temperature, a a constant representing the effect of molecular distortion, and b a constant proportional to the square of the molecular electric moment and representing the effect of molecular orientation. If the gas consists of a mixture of two kinds of molecules defined by N_1, a_1, b_1 and N_2, a_2, b_2 then

$$(\epsilon-1)=N_1a_1+N_2a_2+(N_1b_1+N_2b_2)/T$$

If these two types of molecules correspond to single and to double (associated) molecules and the law of additivity of refractivity be assumed; i.e., $a_2=2a_1$ then

$$\frac{\epsilon-1}{N_1+N_2}=(1+c_2)a_1+[1+(r-1)c_2]\frac{b_1}{T}$$

where $c_2=N_2/N_1+N_2$, the concentration of double molecules and $r=b_2/b_1=\mu_2^2/\mu_1^2$, the square of the ratio of the electric moments of the double and single molecules. As a first approximation it is assumed that the partial pressures of the two constituents can be determined from the ideal gas law which can be stated $p_1=TN_1/273N_0$ where N_0 is the number of gas molecules per cubic centimeter at 0°C and 760 mm Hg. Then

$$p=p_1+p_2=\frac{T}{273N_0}(N_1+N_2)$$

or

$$N_1+N_2=273N_0p/T$$

and the modified Debye equation becomes

$$\frac{(\epsilon-1)T}{273N_0p}=(1+c_2)a_1+[1+(r-1)c_2]\frac{b_1}{T}$$

or

$$\frac{(\epsilon-1)T^2}{273N_0p}=(1+c_2)a_1T+[1+(r-1)c_2]b_1.$$

The concentration c_2 should be determinable from the thermodynamical consideration of equilibrium as Jona[2] has pointed out. According to Planck's[3] expression for chemical equilibrium in gaseous systems

$$c_1^{\nu_1}c_2^{\nu_2}\cdot\cdot\cdot=Ae^{-B/T}T^Cp^{-\nu}$$

or for the simple case of association

$$\frac{c_1^2}{c_2}Ae^{-B/T}T^Cp\,.$$

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[3] Planck, Thermodynamik, 4 Aufl., 1913, § 241, p. 222.

It should be noted here that there is apparently a misprint in Planck's fourth edition at the top of page 223. The statement is made that the conservation of molecular heats requires that $\Sigma\nu_1 C_{p_1}=0$. The correct statement should be $\Sigma\nu_1 C_{v_1}=0$ which is equivalent to $\Sigma\nu_1 C_{p_1}=\Sigma\nu_1$. Accordingly in Jona's article, page 19, Eq. (9) should be $C=1$ instead of $C=0$. This introduces a factor of T which he left out. Even so the principle of conservation of molecular heats seem untenable in view of the equipartition theory. A single molecule of water should have about 6 to 7 degrees of freedom judging from the ratio of the specific heats of steam. According to the quantum theory this would correspond to three degrees of translation and three degrees of rotation completely established and a small amount of vibrational energy for which the classical value is only partially established because of the low temperature. Hence the double molecule would be expected to have about the same molecular heat as the single molecule unless a large amount of vibrational motion is set up at low temperatures. One would then expect C to be considerably greater than unity. C must then be regarded as an indeterminate exponent probably greater than unity. This may be responsible for Jona's lack of agreement for the quantity a/R with Sackur's value.

The fact that C is an indeterminate exponent shows that Jona's extended Clausius-Mossoti equation is not correct as it stands and also that any predictions about association from the variation of the dielectric constant with temperature will be very questionable. However, the latter equilibrium equation suggests an experimental test by the measurement of the variation of the dielectric constant with pressure as follows:

Since $c_1=1-c_2$ the equation for c_2 may be written

$$\frac{c_2}{(1-c_2)^2}=\frac{pe^{B/T}}{AT^C}$$

which shows that c_2 is proportional to p approximately for small pressures and that as the pressure is increased, c_2 becomes less than would correspond to true proportionality. This implies that the curve of $(\epsilon-1)$ plotted against p should be linear or slightly convex from above, and suggests a simple test of the theory, independent of the indeterminate exponent C of T. From the latter equation it should be expected that the association concentration is markedly greater at low temperatures. For this reason a series of measurements were made of the dielectric constant of water vapor varying both the pressure and the temperature. The apparatus outside the experimental condenser was at room temperature so that the maximum pressure that could be used was about 20 mm, the saturation pressure at room temperature. The dielectric constant for these small pressures could be measured fairly accurately because of the large value of the electric moment of water. However, the results are chiefly of qualitative interest and no claim is made to the degree of accuracy obtained in the measurements of the halogen hydrides mentioned above. The method used has been described fully in the above mentioned article on the electric moment of the halogen hydrides. It is a heterodyne beat method using two radio-frequency electron tube generators.

Measurements of Water Vapor

Variation of dielectric constant with pressure. The first measurements were made by allowing almost the full saturation pressure of water vapor to be established in the experimental condenser. Then measurements were made at various pressures pumping out a small amount of water vapor between readings until finally a reading was made for vacuum. The process was repeated in the reverse direction in order to be sure that the effects obtained are reversible and reproducible. In all cases the readings could be reproduced faithfully. Such measurements were made with the experimental condenser at various temperatures, ranging from room temperature up to 165°C. For room temperature, 23.3°C, the data are plotted separately for the sake of clearness; the data for all the temperatures are plotted in Fig. 2. The most striking of all the curves shown is that corresponding to room temperature, 23.3°C, in Fig. 1. A close examination shows that it consists of two nearly linear portions separated by a short transition interval and is similar in appearance to an ionization potential curve. (It immediately suggests itself that the anomalous effect here represented might be the electrical analogy to the effect found by Glaser of pressure variation on the magnetic susceptibility. However, such an effect depends upon the mean free time between collisions, and it would not shift so rapidly with the temperature as is indicated in Fig. 1).

Variation of dielectric constant with temperature. If experimental points on the low pressure rectilinear portions of the various curves are used, it is found that within the limits of experimental error the values of $(\epsilon-1)T^2/273$ plotted against T give a Debye straight line which leads to a value of the electric moment of water vapor consistent with that found by Jona for steam consisting of single molecules. These values are plotted in Fig. 3. The dotted points correspond to values at 17.3 mm Hg, and the crossed points to values at the low pressures. The two lower points on the Debye line are somewhat high, but this deviation might well be due to experimental error since, for the low pressures

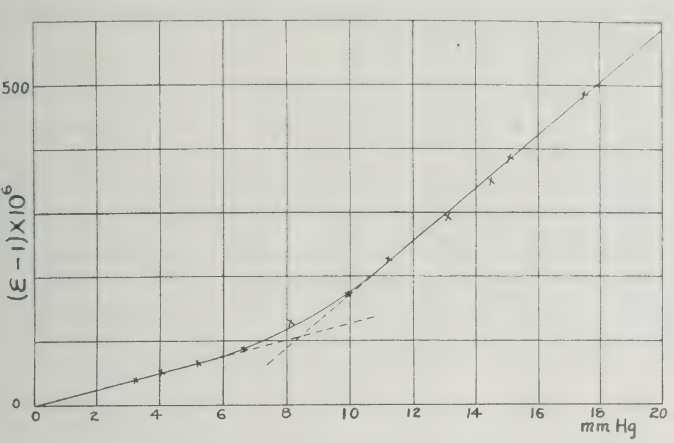

Fig. 1. Variation of $(\epsilon-1)$ with pressure at 23.3°C.

to which these points correspond, the measured capacity change is very small.

It is therefore concluded that what ever the anomalous increase in ϵ is due to, it is practically absent on the lower portion of the pressure

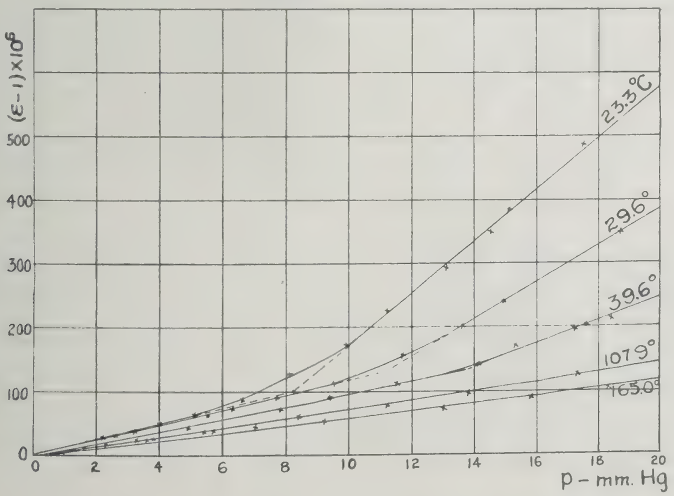

Fig. 2. Variation of $(\epsilon-1)$ with pressure and temperature.

curves. The theory of association outlined above requires that the curve in $(\epsilon-1)$ and p be rectilinear or slightly convex from above, whereas the experiment curve is decidedly concave. Hence Jona's explanation by association into double molecules seems inadequate to explain these observations. One might explain the observed slope of the curve of Fig. 1 on the assumption of association into triple molecules in which case the equilibrium equation is

$$\frac{c_3}{(1-c_3)^3}=\frac{p^2e^{B/T}}{AT^C}$$

This would give a curve in $(\epsilon-1)$ and p concave from above, and the approximation to a straight line might be explained as due to a compensation of the increase in $(\epsilon-1)$ due to the term p^2 and the effect produced by the increasing importance of the expression $(1-c_3)^3$ as c_3 becomes large. Now vapor density measurements on water vapor preclude the possibility of association to any degree greater than a few percent at most, whereas if one assumes any reasonable value for the moment of the double or triple molecule (Jona assumed that the moment doubled on association) it requires large percentages of association to account for the observed dielectric constants. For example, if one supposes the associated molecule to have four times the moment of the single molecule, it requires about 10 percent association. This fact makes the interpretation on the basis of association seem very doubtful.

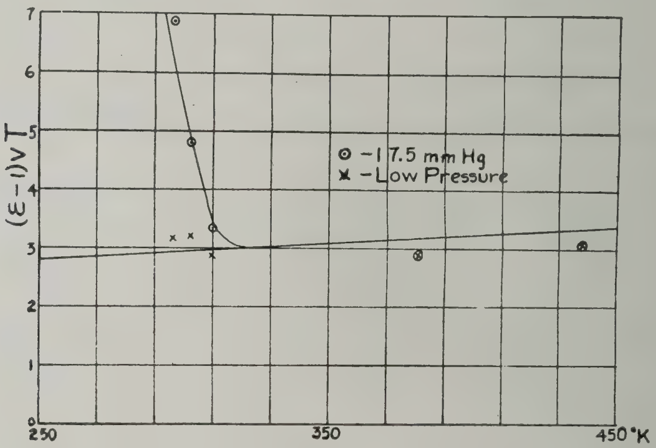

Fig. 3. Variation of $(\epsilon-1)T^2/273$ with temperature.

SURFACE LAYERS AND THE DIELECTRIC CONSTANT

An alternative to the assumption of association is to suppose the effect to be due to adsorption of a layer of water on the surface of the condenser plates. It is a well known fact that the surface tension of films of water decreases when the film thickness becomes less than a certain minimum. This is explained by supposing that this minimum thickness is equal to the radius of the sphere of molecular atrraction. When the thickness of the film becomes less than this radius the surface tension is less than the normal value because there are fewer molecules in the sphere of attraction. Accompanying this lower surface tension there is, therefore, a greater vapor pressure. If, however, the film is adsorbed on the surface of a substance such as a metal, which it wets (i.e. a substance having great attraction for the molecules) the reverse state of affairs should be expected. The sphere of molecular attraction for a molecule in the free surface of the film contains some of the metal molecules and consequently the attraction is greater than if it contained all water molecules. The surface tension should be abnormally high and the vapor pressure should be low since the increased attraction reduces the number of molecules escaping per second.

Condensation of this sort might be regarded as a limiting case of capillary adsorption where the curvature of the adsorbing surface vanishes. Capillary adsorption below the saturation pressure must be due to the fact that for great curvature of a surface the attraction for a molecule must be increased. There is fundamentally no difference in the two kinds of adsorption. The chief difference is that for a curved surface the adsorption forces are greater.

An upper limit to the thickness of such layers is the radius of the sphere of molecular attraction of the metal molecules for a water molecule, and should be of the order of magnitude found by Rücker for soapy water. Furthermore, the thickness of the film at saturation pressure should be equal to this limiting value. This thickness can be calculated approximately from the data of Fig. 1. Let t be the distance between the condenser plates and d the thickness of the adsorbed water layer (both plates). The experimental value of t was .05 cm. Hence d will be small compared with t. The apparent change in the condenser plate separation on the insertion of a slab of thickness d and dielectric constant K is $d(1-1/K)$ if the original dielectric constant is only negligibly different from unity. If K is large the apparent change is approximately equal to the actual thickness of the slab.[4] Hence d/t is the apparent fractional change in plate separation. This must equal the apparent fractional change in ϵ over what it would be if the lower part of the curve of Fig. 1 were extended to the saturation pressure.

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[4] Possibly the dielectric constant of such a layer of water is different from the ordinary dielectric constant, but one would expect only a small difference. At any rate the importance of K is small. For $K=80$ as for ordinary water an error of only a little more than one percent is made in neglecting $1/K$.

In this manner d is found to be 1.65×10^{-5} cm. Since this includes the films on both plates the actual film thickness is 8.25×10^{-5} cm. This agrees very well with the minimum thickness of soap films of from 4.5 to 9.5×10^{-5} cm found by Rücker and Reinhold.[5]

The fact that the apparent radius of the sphere of molecular attraction is about 100 to 200 molecules long is not necessarily in contradiction with the fact that the force due to an individual molecule is not appreciable at distances farther than a few molecular diameters at most. In a substance like water, whose dielectric constant is very large, the field of force due to a single molecule should induce orientations in the surrounding molecules and this orientation in turn would set up an additional field for molecules farther out and so on. In this manner the force on a single molecule might depend upon induction effects which it produces many molecules away from itself. The distance at which this induction effect is inappreciable is to be regarded as the apparent radius of molecular attraction.

Consider now the phenomena which might take place as the pressure of the water vapor is increased from vacuum. Two types of adsorption might take place: first, the type where the molecules are held rigidly (similar to solid molecules); and second, the type where the molecules are free to move about and be oriented easily by an electric field (liquid molecules). So far as can be told from these measurements there may be no adsorption of the first type at all, and if there is any it seems probable from experiments[6] on monomolecular oriented films that there is only one such layer. As regards the subsequent formation of liquid layers over this solid layer the solid layer would behave essentially as the metal, so that it will not be considered in what follows. Edser[7] has shown that about 94 percent of the surface energy of a liquid resides in the first layer. Consequently after the formation of the first liquid layer on a metal surface the surface energy should be of the same order of magnitude as the normal liquid surface energy. Likewise the vapor pressure above this layer should be of the ordinary order of magnitude but somewhat less because of the increased attraction by the metal molecules. After this the change in pressure with thickness depends on the fact that as the film gets thicker the distance of the surface water molecules from the more strongly attracting metal molecules becomes greater. Conversely, as the vapor pressure increases from vacuum, a single liquid layer will be established only after the pressure has reached

[5] Rücker and Reinhold, Phil. Trans. **177**, 2, 627 (1886).

[6] See Taylor's Physical Chemistry, vol. I, p. 136.

[7] E. Edser, 4th British Assoc. Report on Colloid Chemistry, p. 94.

a definite value somewhat less than the ordinary vapor pressure of water, but of the same order of magnitude. As the pressure is increased still further, the layers will form rapidly. As regards the electrical effect produced in the present measurements, the water would virtually start to condense at this definite pressure since the first layer would have a negligible effect on the apparent deliectric constant. Thus an explanation is given for the apparent critical pressure observed in Fig. 1. The general behavior of the curve is, then, qualitatively according to what would be expected.

SURFACE CONDENSATION AND KINETIC THEORY

So far the question of surface condensation has been regarded from the point of view of the properties of liquids. It was seen that the existence of a condensed surface layer in the liquid state is palusible from the properties of liquids. Such a condensed layer can also be predicted from the kinetic theory of gases in an interesting manner.

From Jona's work and the present data, water is known to have a large electric moment, 1.8×10^{-18} e.s.u. As such a molecule approaches a metal surface it will be attracted by electric induction which can be represented by the mirror image of the doublet in the surface of the metal.[8] As a result of this attraction there will be an increased concentration of the molecules near the metal surface. The potential energy of a doublet inclined at an angle θ to the normal and at a distance x from the surface is by simple electrostatics

$$W = -\mu^2 \cos^2 \theta / 8x^3$$

Applying Boltzmann's theorem for the distribution of molecules:—

$$dn = Ae^{\mu^2 \cos^2\theta / 8x^3KT} \sin \theta d\theta$$

$$= Ae^{a \cos^2\theta} \sin \theta d\theta \qquad \text{where } a = \mu^2/8x^3kT$$

The total number of molecules per cc at a distance x

$$N_x = A \int_0^\pi e^{a \cos^2\theta} \sin \theta d\theta = -2A \int_0^1 e^{ay^2} dy$$

For $x = \infty$, $a = 0$ and

$$N_\infty = -2A$$

$$\therefore N_x = N_\infty \int_0^1 e^{ay^2} dy$$

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[8] Richardson, Schottky, Langmuir, and Dushman have used this idea in relation to the work function for an electron leaving a metal surface.

or

$$p_x/p_\infty = N_x/N_\infty = \int_0^1 e^{ay^2}dy$$

where p is the pressure. This probability integral can be evaluated in series

$$N_x/N_\infty = \left[1+\frac{a}{3}+\frac{a^2}{10}+\frac{a^3}{46}+\frac{a^4}{216}+\frac{a^5}{1200}+\cdot\cdot\cdot\right].$$

The concentration N_x thus increases as the surface is approached. As the doublet approaches the metal surface to within distances of molecular magnitude, the above integral will not hold but will have to be replaced by some unknown function which includes the repulsive effects of the electronic orbits at collision. Then, assuming that a negligible amount of molecules penetrate into the metal lattices, N_x/N_∞ follows the above integral until the repulsive effects are appreciable after which it goes through a maximum and falls to zero at the point of nearest approach of the water molecules.

While the statistical equation cannot be applied for points very near the metal surface, it ought, nevertheless, to be possible to determine the order of the magnitude of the concentration produced by the adsorption forces. A limit will be set on x by the distance of nearest approach of the water molecule. If the metal molecule were fixed in space during a collision of the water molecule, this lower limit would be approximately equal to the molecular radius, but since the metal molecule must be moved in the direction of impact, this limiting value of x may be somewhat less than the molecular radius. Although the repulsive forces at collision change the shape of the actual curve for N_x/N_∞ the maximum value of N_x/N_∞ should be of the same order of magnitude as the value of N_x/N_∞ calculated from the probability integral for x equal to the distance of nearest approach.[9] If it be supposed that condensation in more than a single layer cannot exist until the actual maximum value of N_x exceeds the ordinary saturation concentration, the order of magnitude of the distance of nearest approach can be calculated from the above integral. Setting p_x equal to the pressure plotted in Fig. 1, at the point where deviations become appreciable $N_x/N_\infty = p_x/p_\infty = p_s/p = 20.0/6.2 = 3.2$ approximately. The value of a corresponding to this value of N_x/N_∞ can be found by approximation to be about 2.5. Then x can be found from:

$$x^3 = \mu^2/8KTa$$

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[9] Cf. Langmuir's discussion of the work function for thermionic emission, Trans. Amer. Electrochem. Soc. **29**, 161 (1916).

taking $\mu = 1.8 \times 10^{-18}$, $K = 1.346 \times 10^{-16}$, and $T = 300°\mathrm{K}$. In this manner x is found to be approximately 2.2×19^{-8} cm, which is a little greater than the molecular radius of water.[10] Hence the result is in good accord with the above considerations.

According to this view for any given value of pressure p_∞ the maximum value of N_x should be limited by the distance of nearest approach, or by the size of the molecule. In the above rough consideration the doublet was considered as concentrated at the center of the molecule. Now if the doublet is concentrated on one side of a molecule; i.e., if the molecular field is strongest on one side, the maximum value of N_x should be greater than if the doublet were concentrated at the center of the molecule. For example, such might be expected to be the the case where there is an OH group in the molecule. In general the values of the critical pressure, shown in Fig. 1, for various substances might give qualitatively some knowledge of the distribution of the electric moment within molecules.

In a similar manner condensation should take place on dielectric surfaces. (The induced image is $-\mu(K-1)/(K+1)$ in this case.) There is in fact experimental evidence for this. Professor Menzies[11] gives a value of about a micron for the thickness of such layers on glass. In the case of glass, complications are introduced by solution in the alkali constituents of the glass. This process should be slow. Menzies' results show a change in absorption with time, which is in accord with the supposition that there are both an "instantaneous" effect like that for a metal surface and a volume absorption which takes a long time to reach equilibrium.

Conclusions

The results of the experiments here described are of interest from the points of view of both the dielectric constant and adsorption. The apparent anomaly in the behavior of the dielectric constant of water vapor is probably not due to association as supposed by Jona, but to surface condensation produced by molecular attraction. Probably all of the anomalous values of dielectric constant measured by Jona are due to this surface condensation. If the deductions of the foregoing discussion on surface layers are correct, these anomalies could be avoided by measuring dielectric constants only at pressures below the critical condensation pressure, which could be found experimentally. (This will probably depend considerably on the particular metal used for the condenser plates.) The difference between the author's measurements on SO_2, etc., and those of Jona may be due to different surface conditions of the condenser plates.

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[10] Kaye and Laby, Physical and Chemical Constants, p. 35.

[11] A. W. C. Menzies, Jour. Amer. Chem. Soc. **42**, 10, 1952 (1920).

The properties of the adsorbed liquid layer of water postulated above may be summarized as follows. As the number of adsorbed liquid molecules approaches the number corresponding to a mono-molecular layer, the vapor pressure rises rapidly until it reaches a value somewhat less than the ordinary vapor pressure of water. After this, as the number of molecules increases, or as the thickness of the film increases (since now there are many layers), the rate of change of pressure with thickness drops rapidly to a final constant value (Fig. 1).

If n be the number of adsorbed molecules and p the vapor pressure, then as p increases to the ordinary saturation pressure n will first increase to the negligibly small number in a monomolecular layer while p increases to a virtual critical value less than the ordinary vapor pressure. Then as p increases further n increases rapidly reaching a uniform rate of increase just above the critical pressure. Correspondingly dn/dp is practically zero until the critical pressure is reached, after which it rises rapidly to a constant value which it retains up to the final saturation point. The final thickness of the layer is of the order of several microns, which corresponds to about two hundred molecular layers.

In conclusion the author wishes to express his indebtedness to Prof. K. T. Compton for his valuable advice and criticism in this investigation.

National Research Fellowship,
Princeton University,
December 11, 1925.

MARCH, 1926 PHYSICAL REVIEW VOLUME. 27

ON THE QUANTITATIVE THEORY OF AN ELECTROSTATIC VOLTAGE MULTIPLIER

By A. W. Simon[1]

Abstract

The detailed quantitative theory of a symmetrical, four carrier, electrostatic voltage multiplier is developed. It is shown that a machine of this type steps up a given applied d.c. potential in a definite ratio, and a formula for this (transformation) ratio is deduced in terms of the coefficients of capacity and the coefficients of induction of the elements of the machine in a definite configuration. A formula which gives the potential of the receivers every geometrical cycle (quarter turn) is deduced. While the current furnished by a device of this sort is extremely small, it may be used separately to excite an ordinary static machine, so that this machine will give a constant current at a constant high potential.

IT HAS been pointed out in a previous paper[2] that the method of attack used in developing the quantitative theory of the static machine can be applied also to an electrostatic voltage multiplier.[3] The present work is concerned with the detailed analysis of a simple machine of this type.

The machine studied is represented diagramatically in Fig. 1. It consists of two inductors 7, 8, on which are impressed the constant voltages $+E$ and $-E$ respectively; two receivers 5, 6; and four revolving carriers 1, 2, 3, 4. The neutralizing rod 9 and the midpoint of the battery are connected together and grounded.

The action of the machine is seen readily from the figure. When the carriers are in the positions 1, 2, a charge of sign opposite to that of the inductor near which it happens to be is induced on each carrier, these charges are then carried forward and shared with the receivers, and so forth.

In practice such a device will charge the receivers to a difference of potential which is much greater than that applied to the inductors, and so is a sort of direct current transformer, although actually the increased potential comes from the work done in separating charges of opposite signs, i.e. is the result of a generating action rather than of a transformer action.

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[1] National Research Fellow.

[2] A. W. Simon, Phys. Rev. **26**, 111 (1925).

[3] A. W. Simon, J. Opt. Soc. Am. **10**, 669 (1925).

Our problem is to follow the action of this machine quantitatively. If we use the same notation as that employed in previous papers,[4] with the one modification that instead of denoting the geometrical cycle by a subscript we write it as the argument of the functions Q and V, we have as the fundamental equations for the charges for two successive geometrical cycles:

$$Q_5(n+1)+Q_3(n+1)=Q_5(n)+Q_1(n) \tag{1}$$

$$Q_6(n+1)+Q_4(n+1)=Q_6(n)+Q_2(n)\ . \tag{2}$$

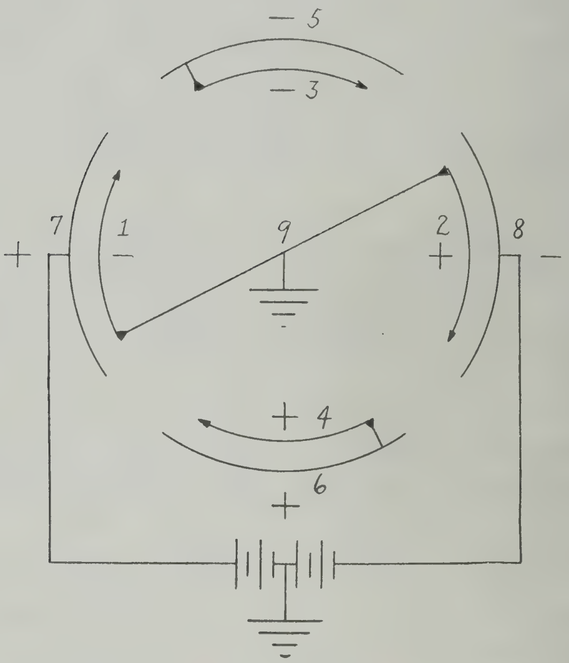

Fig. 1. A four-carrier, direct electrostatic voltage multiplier of the symmetrical type.

If now we substitute for each of the Q's its value in terms of the corresponding potentials and electric coefficients, and note that we have two-fold electrical symmetry, we obtain:

$$aV_3(n+1)+bV_5(n+1)+cE=a'V_3(n)+b'V_4(n)+c'E \tag{3}$$

$$bV_3(n+1)+aV_5(n+1)-cE=b'V_3(n)+a'V_4(n)-c'E \tag{4}$$

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[4] For details both as to notation and general method employed in this paper, the reader must be referred to the author's previous work on the theory of the static machine, in particular to Phys. Rev. **24,** 690 (1924); **25,** 368 (1925); **26,** 111 (1925).

where a, b, c, a', b', c', are given by:

$$a = a_{35,35} = a_{64,64} \qquad a' = a_{35,51} = a_{64,62}$$

$$b = a_{64,35} = a_{35,64} \qquad b' = a_{64,51} = a_{35,62}$$

$$c = a_{7,35} - a_{8,35} = a_{7,64} - a_{8,64} = 0 \qquad c' = a_{7,51} - a_{8,51} = a_{7,62} - a_{8,62}\ .$$

The solution of Eqs. (3) and (4) is:

$$V_3(n) = C_1 r_1^n + C_2 r_2^n + C_3 \tag{5}$$

$$V_4(n) = C_1' r_1^n + C_2' r_2^n + C_3'\ , \tag{6}$$

where the C's and r's are given by the following:

$$C_1 = C_1' = \tfrac{1}{2}\big(V_3(0) + V_4(0)\big) \tag{7}$$

$$C_2 = -C_2' = \tfrac{1}{2}\big(V_3(0) - V_4(0)\big) - \rho E \tag{8}$$

$$C_3 = -C_3' = -\rho E = -\big(a_{71} - a_{81}\big)E/\big(a_{35,3} - a_{35,4}\big)\ . \tag{9}$$

$$r_1 = \big(a_{35,51} + a_{35,62}\big)/\big(a_{35,35} + a_{35,64}\big) \tag{10}$$

$$r_2 = \big(a_{35,51} - a_{35,62}\big)/\big(a_{35,35} - a_{35,64}\big)\ . \tag{11}$$

With regard to the magnitudes of r_1 and r_2, it is possible to prove the following relation from the general properties of electric coefficients:

$$0 < r_1 < r_2 < 1$$

Let us now turn to the physical interpretation of these results. Taking account of (5), (6), (9), and (12), we note that both $V_3(n)$ and $V_4(n)$ approach constant values as n approaches infinity. In particular, we have:

$$\begin{aligned} \mathop{Lim}_{n\to\infty}\ V_3(n) &= V_3(\infty) = -\rho E \\ \mathop{Lim}_{n\to\infty}\ V_4(n) &= V_4(\infty) = +\rho E\ . \end{aligned} \tag{13}$$

The quantity ρ represents the transformation ratio of the machine, and it is of interest to investigate on what this ratio depends and how it may be varied. For this purpose Eq. (9) is rewritten as follows:

$$\rho = -\big(a_{71} - a_{81}\big)/\big(a_{33} + a_{53} - a_{43} - a_{63}\big)\ . \tag{14}$$

In order to make ρ large, we must surround the carrier as completely as possible in position 1 thus making a_{71} large and a_{81} very small; we must also surround the carrier as completely as possible in position 3, thus making a_{53} almost equal in absolute value to a_{33}, and both a_{43}

and a_{63} small.[5] In the limit, if the carrier in position 3 were completely surrounded, i.e. if $a_{33}=-a_{53}$, and $a_{43}=a_{63}=0$, the transformation ratio would become infinite. It is interesting to note that this would occur even though the carrier were not surrounded in position 1. In this respect our machine is an exceptional case, for ordinarily to produce an infinite ratio, the carriers must be surrounded completely in both positions. The explanation in our case is that since the potential of the receivers eventually become equal and opposite Eq. (13) their effect on the carrier when the latter receives its charge (position 1) is exactly zero, so that no matter how highly the receivers become charged, they do not counteract the effect of the inductors.

Another important point to note is that the capacity coefficient a_{55} does not appear in the expression for ρ Eq. (14). This means that the transformation ratio does not depend on the capacity of the receivers or any capacities connected to the receivers. In other words, the transformation ratio is independent of the load.

Let us next inquire how the machine builds up. For this purpose Eqs. (5), (6), (7), (8), are of value. We can assume of course that the receivers are originally charged to any potentials whatever. However, two cases are of special interest. (1) The receivers 5, 6, are originally charged to potentials $-\rho E$ and $+\rho E$ respectively. For this case we obtain $C_1=C_1'=C_2=C_2'=0$, i.e. no change takes place, as we should expect. (2) The receivers originally have equal but opposite potentials. For this case we obtain $C_1=C_1'=0$, i.e. only the r_2 terms are effective in building up. The r_1 terms therefore represent the tendency for the two receivers to attain equal and opposite potentials, and this occurs even before these potentials have reached their final values, for from inequality (12) it is seen that the r_1 terms represent transients of shorter duration than the r_2 terms.

We have so far spoken of the machine as building up. In particular, however, if the original potentials are higher than the equilibrium (final) potentials, it is also evident from the equations that the machine will build "down," again with an r_1 transient, if the original potentials are not equal and opposite, or none if they are, etc.

In conclusion a word must be said with regard to the currents furnished by devices of this sort. Strictly speaking, a device of the type just discussed can be used only for charging a condenser, not for furnishing steady currents through a resistance. But even for capacity loads, due to the fact that the capacities involved in the machine itself are small, the currents attained are usually of the order of microamperes, so that a device of this sort is inferior even to the ordinary static machine. However, a modified device can easily be constructed, which will not be inferior to the static machine in this respect, and, furthermore, furnish a constant and a controllable potential across a (high) resistance. For this purpose we have merely to impress the constant high potential furnished by an electrostatic voltage multiplier on the inductors of a static machine of the Holtz type (the inductor brushes being removed) and connect the resistance across the terminals. By this means not only more or less continuous currents can be produced, depending on the size of the sectors of the static machine and the resistance of the load, but also these currents are comparable in magnitude with those furnished by the ordinary static machine. Used in this way, the static machine becomes essentially a separated excited electrostatic generator, and as such has the advantages that it is a constant potential machine and that its output voltage can be controlled. So far no experiments along this line have been made, but they would be of interest.

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[5] It is of course always assumed that the geometrical symmetry of the machine is preserved, i.e., that the carrier in position 2 is treated exactly the same as that in position 1, the carrier in position 4 exactly the same as that in position 3, and so on.

Norman Bridge Laboratory,
California Institute of Technology,
Pasadena, California.
December 1, 1925.

MARCH, 1926 PHYSICAL REVIEW VOLUME 27

ANOMALOUS ACTION OF THE RAYLEIGH DISK

By Charles H. Skinner

Abstract

Torque on Rayleigh disk in a resonating tube, for high pitch sounds.—In the case of a disk 15 cm in diam. in a tube 16 cm in diam., a study of the deflection as a function of wave-length, 4 to 28 cm, showed that for a wave-length of 28 cm the disk tended to set itself parallel to the axis of the resonator, and hence was deflected in a direction opposite to the usual one. Other negative maxima were observed for waves of about 14 and 7 cm. Experiments with smaller disks showed that beyond a certain tube length the maximum critical wave-length for a negative maximum is independent of tube length and depends more on tube diameter than on disk diameter, approaching twice the tube diameter as the size of the disk is increased nearly to that of the tube.

During an investigation with a Rayleigh disk[1] of the energy output of a variable whistle blown with constant air pressure, it was observed that as the pitch of the whistle passed through a certain critical value, the deflection of the disk reversed in direction. This is not in accordance with the usual action.

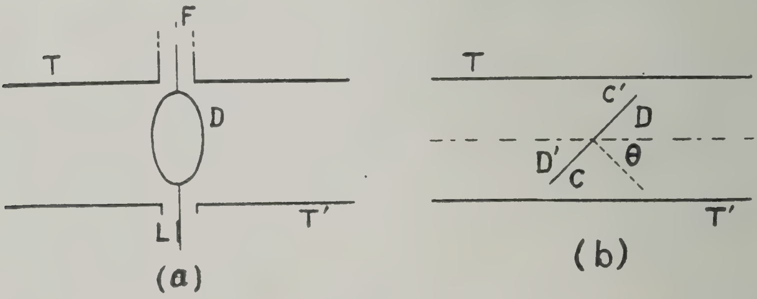

Fig. 1.

In order to investigate the conditions attending this anomalous action, a modification of Rayleigh's original arrangement was adopted as shown in Fig. 1 (a). A circular disk D cut from thin sheet mica was suspended at the middle of a horizontal cylindrical tube TT' by means of a quartz fiber F. A light capillary glass tube carrying a mirror L was attached to the lower part of the disk and extended downwards in line with the suspension, so that deflections could be observed by means of a telescope and scale. The initial angle θ between the normal to the disk and the axis of the tube was 45°. The tube was open at each end except for a layer of cheese-cloth which served to protect the disk from troublesome air currents. At a point on the extension of the axis of the tube was placed the source of sound.

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[1] Rayleigh, Phil. Mag. **14**, 186 (1882).

When the whistle was in operation, the disk was deflected until the restoring couple set up by the twisted fiber balanced the turning moment of the sound waves. The relation between the wave-length and deflection is shown in Fig. 2, which is a typical curve for wave-lengths ranging from two-thirds to three times the diameter of the disk. The deflection of the disk is considered positive if the angle between the normal to the disk and the axis of the tube decreases. If the angle increases, the deflection is considered negative. In obtaining this curve, the length of the tube was kept constant. Thus the tube would be in resonance for certain wave-lengths only. This explains the positive maxima at *A* and *B*, which are seen to be approximately an octave apart. The negative maximum at *M* corresponds to a wave-length not quite twice the diameter of the disk. The other negative maxima at *N* and *P* are not well defined, but they appear to correspond to wave-lengths which are slightly less than the diameter and half the diameter, respectively. It thus appears that the anomalous deflections are due to resonance between the incoming waves and the space enclosed between the disk and the walls of the tube.

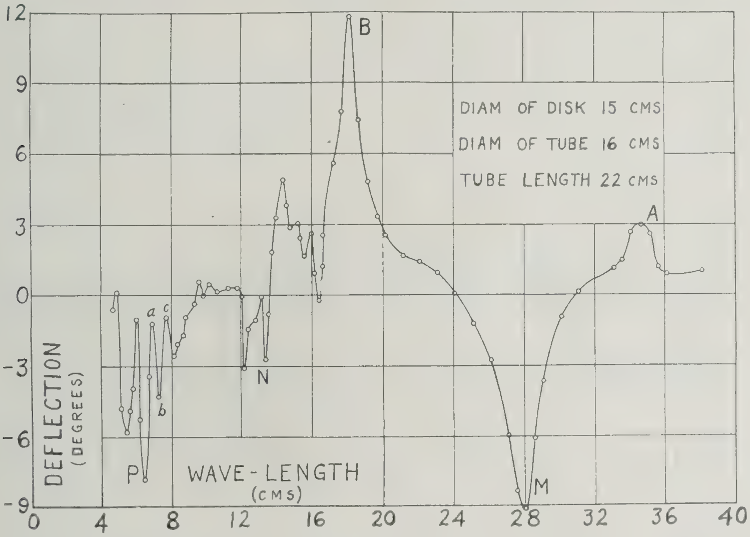

Fig. 2. Variation of angular deflection of the Rayleigh disk with wave-length of the sound.

In addition to the maximum positive and negative deflections noted above, there are a number of maxima and minima following each other closely, especially in the region of shorter wave-lengths, as at *a*, *b* and *c*. These are probably due to changes in the sound pattern, or standing waves, in the room, as the frequency changes, causing a succession of nodes and loops to pass across the disk.

The wave-length L_m corresponding to the negative maximum at *M* varies with the relative dimensions of the disk and tube in which the the disk is mounted, as shown in Fig. 3. Curve (*a*) shows how L_m varies with the length of the tube; (*b*), how L_m varies with the diameter of the tube; while (*c*) shows how L_m varies with the diameter of the disk. It is seen from curve (*a*) that L_m is independent of the length of the tube after the latter is four or five times the diameter of the disk; and from curves (*b*) and (*c*), that L_m is approximately twice the diameter of

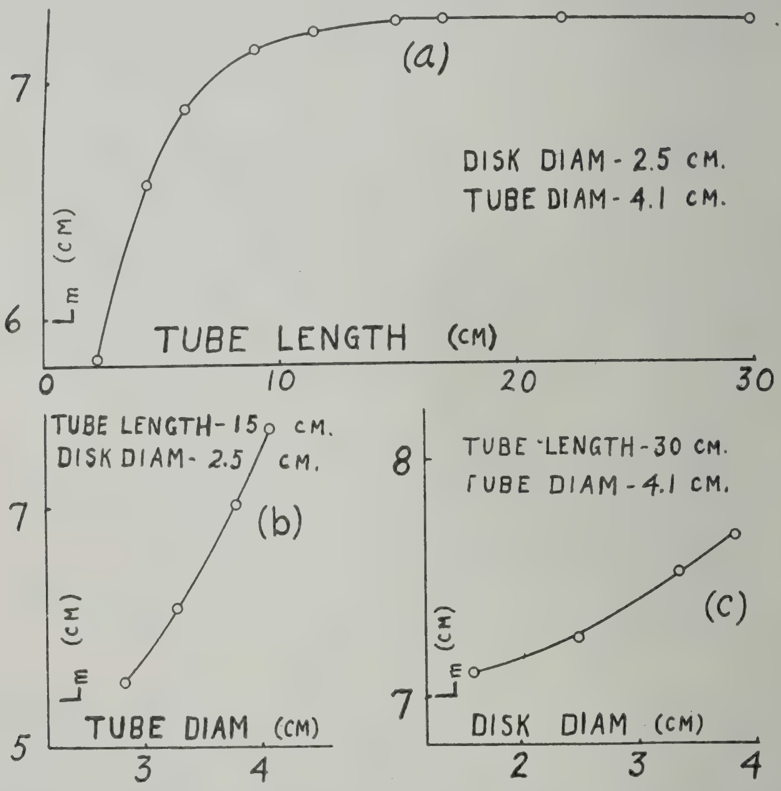

Fig. 3. Variation of the wave-length of sound producing a maximum negative deflection of the Rayleigh disk with (a) tube-length, (b) tube-diameter, and (c) disk-diameter.

the disk when the latter is slightly less than the diameter of the tube. Further experiments have shown that L_m is independent of the position of the disk in the tube, as long as it is not near an end; also that it does not depend on whether the tube is open at each end or closed, nor on the intensity of the sound.

Similar results have been obtained with rectangular disks mounted inside of tubes of rectangular cross-section. However, if the disk is mounted in the open air or within tubes whose walls are removed a short distance from the disk, no negative deflections are obtained.

In general, then, when a disk enclosed within a tube is acted on by sound waves, there are two opposing forces tending to produce rotation. The one is somewhat analogous to that which acts on any flat object in a current of air tending to set the object at right angles to the current; while the other is brought into play as a result of resonance in the space between the disk and the walls of the tube. The first force tends to set the disk at right angles to the axis of the tube; the second, parallel to the tube.

König[2] developed from hydrodynamical principles the following expression for the moment M due to the action of the first force on a circular disk when placed in the path of a train of sound waves but not enclosed on any side:

$$M=\frac{4}{3}da^3W^2\sin 2\theta$$

in which d is the density of the air, a the radius of the disk, W the average velocity of the vibrating air particles due to the sound waves, and θ the angle between the normal to the disk and the direction of vibration. This expression is usually considered as applying also to a disk mounted within a resonator. If the disk is deflected until the restoring couple produced by the twisted suspension just balances the torque set up by the vibrating air, then it follows from the above equation that intensities are proportional to deflections if the latter are small.[3] It is evident, however, that for waves of the order of the diameter of the disk and less in length, the motion of the vibrating air at one part of the disk may be opposite in direction from the motion at another part, so that the resulting torque tending to produce rotation in the positive direction may be less than would be produced by long waves of the same intensity. That is, the deflections are not proportional to intensities for wave-lengths of the order of the diameter of the disk and less, even when the disk is not confined within a tube. König's expression, therefore, should include a term involving wave-length.

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[2] W. König, Wied. Ann. **43,** 43 (1891).

[3] F. R. Watson, Phys. Rev. **7,** 125 (1916).

In regard to the second force mentioned above, consider the space included between the disk and the walls of the tube. This space forms a resonator somewhat analogous to a conical horn. At resonance, the energy density at C and C', Fig. 1 (b), is greater than at D and D'. Thus the torque tending to produce rotation in the negative direction will be a maximum for the wave-lengths for which the enclosed space responds with maximum resonance with the incoming sound waves. If this torque is greater than that due to the first force mentioned, rotation in the negative direction will result.

From the preceding, it is clear that the Rayleigh disk inside a tube cannot be used for comparing the intensities of sounds whose wave-lengths are comparable to the diameter of the disk. The effect tending to produce a negative deflection is very small for long wave-lengths because of the lack of resonance in the space between the disk and the walls of the tube, and König's theory may be considered as giving a close approximation for the resultant couple acting on the disk. The instrument, however, must be used with caution, for if there is an overtone present whose wave-length is such as to produce a negative torque on the disk, the resulting deflection will not be proportional to the incident sound energy.

The writer wishes to express his appreciation to Professor Foley and other members of the Physics Department of Indiana University for equipment and friendly cooperation during the above investigation.

Ohio Wesleyan University,
December, 1925.

BOOK REVIEWS

Radioactivity. By A. F. Kovarik and L. W. McKeehan, Bulletin of the National Research Council, Vol. 10, No. 51.—This book is part of a report of the National Research Council Committee on X-rays and Radioactivity. The authors have not endeavored to present a textbook on the subject of radioactivity, but to bring to notice, and to comment upon, research work which has been published since the year 1916. This date was chosen for the reason that in that year there appeared the well-known book of Meyer and von Schweidler, "Die Radioaktivität," and this contains an almost complete list of references to papers which were published before 1916. In this report the authors have tried to include a mention of every paper on a radioactive subject which has appeared between 1916 and the end of June, 1924. Some publications of later date have also been referred to, where these were of special interest. Papers of doubtful value or importance have not been excluded. The result of this procedure is a completeness in the references to original papers which could hardly be surpassed. The literature has indeed been searched with remarkable thoroughness, and this completeness is the most striking feature of the book. The author's thoroughness in this respect has, however, brought with it the disadvantage that to one not conversant with the subject the present position is sometimes rather vaguely sketched in, for the number of papers referred to is so great that a detailed critical survey was not always possible. The report consists of 203 pages, 30 pages of which are taken up by the index, which refers to some 1500 papers mentioned in the text. It is clear that comment on the papers has been reduced to a minimum, and in some cases it is perhaps too brief to bring out the relative value and importance of the papers.

In the introduction the authors propose a new and a more rational system of nomenclature for the radioactive bodies. On this system a radio-element is defined by its atomic number and the chemical symbol of the principal member of its series. Isotopes of the same series are distinguished by a Roman numeral indicating the order in the series. To show the general scheme we may quote the table given for the radium series.

Ionium	Io	90Ra
Radium	Ra	88Ra
Radon (Radium emanation)	Rn	86Ra
Radium A	RaA	84RaI
Radium B	RaB	82RaI
Radium C	RaC	83RaI
Radium C′	RaC′	84RaII
Radium C″	RaC″	81Ra
Radium D	RaD	82RaII
Radium E	RaE	83RaII
Radium F (Polonium)	RaF	84RaIII
Radium G	RaG	82RaIII

The proposed system has many advantages over the present nomenclature, which is in some cases rather confusing, but it may be doubted whether the gain in simplicity would be sufficient compensation for the loss of the historical interest and association of the names now in use.

The first chapter deals with the radioactive transformations. Since 1916 two new elements have been discovered and the decay constants of others have been redetermined. Then follow three chapters dealing with the α, β, and γ rays. These chapters are naturally the most important in the report, and the literature is discussed in some detail. They are followed by short chapters entitled Nuclear Structure and Radioactive Processes, Radioactivity in Geology and Cosmology, and The Effects of Radioactive Radiations upon Matter. Some of the points considered in these later chapters are dealt with very summarily, and little comment is made upon the papers quoted.

At the end of every chapter there are given tables summarising as far as possible the information dealt with in the text. The tables in the chapters on the radiations are extremely useful, for they contain a large amount of detailed information. In Table IIIA, p. 68, and IIID, p. 70, it is stated on the authority of Bates and Rogers that RaC emits α-particles of 3.8 cm range. These α-particles have not been observed. Their existence is deduced from a knowledge of the transformation series, and their range is calculated from the Geiger-Nuttall relation. The tables of the β-ray and γ-ray spectra suffer from the fact that in some cases the same line, measured by different observers naturally with small discrepancies, receives different designations. It is thus somewhat difficult to form an idea of the actual number of different lines which have been found in the β- and γ-ray spectra of the radio-elements.

These, however, are comparatively small faults in a book which covers such an enormous range in so small a compass. The great virtue of the book is its remarkable thoroughness in the scrutiny of the literature, a thoroughness which can hardly be over-emphasized. This alone will make the report of great value and use to workers in radioactivity, and even those most conversant with the subject will find here references to papers which had hitherto escaped notice. The thanks of all workers in this field are due to the authors for carrying out a heavy and difficult task in so thorough a way.—Pp. 203, National Research Council, Washington, D. C., 1925.

J. CHADWICK.

Dynamical Theory of Sound: Second Edition. HORACE LAMB.—The publication of the first edition of this book in 1910 met a real need for a condensed and concise presentation of sound from the dynamical point of view. As such, it has been recognized as a standard text on the subject, along with the more comprehensive treatises of Rayleigh and Helmholtz. A review of the new edition may therefore be confined to such changes and additions as are noted.

This is not a heavy task. The changes are limited to corrections of slight textual errors. The additions comprise about five pages in all, mostly descriptive in character devoted to the following topics: Approximate Determination of Free Period, Aeolian Tones, Acoustic Properties of Buildings, Doppler's Principle, Multiple Resonance, and the Hot Wire Resonator.

One notes the dearth of new material with a feeling of distinct disappointment. The fifteen years between the publication of the first and second editions have marked greater advancement in the field of applied acoustics than the entire half century preceding. Important practical applications to the problems of airplane detection, submarine signalling, wired and wireless telephony, phonographic reproduction and the control of sound in buildings have all come during this latter period, and it is to be said that most of these have come by laborious experimentation without the guidance of adequate dynamical theory. One feels that the concept of acoustic impedance, introduced by A. G. Webster, and applied by him to the problem of horns and resonators, by Kennelly in telephonics and by Brillie to the propagation of waves in solid and liquid media could have been illuminatingly treated by Dr. Lamb in a chapter of the new edition. But perhaps the author's basis of selection of subject matter was the dictum "What is not found in Rayleigh is not Sound." Pp. viii+307. Longmans, Green and Co., New York City, 1925. Price $6.00.

PAUL E. SABINE.

Second Series *April, 1926* *Vol. 27, No. 4*

THE
PHYSICAL REVIEW

HIGH FREQUENCY RAYS OF COSMIC ORIGIN
I. SOUNDING BALLOON OBSERVATIONS AT EXTREME ALTITUDES

By R. A. Millikan and I. S. Bowen

Abstract

Discharge rate of an electroscope at altitudes from 5 to 15.5 km.—Four specially designed instruments, each comprising a recording electroscope, thermometer and barometer and each weighing but 190 gr were sent up with sounding balloons from Kelly Field, Texas. Three were recovered and of these two had satisfactory records of their flight during which they reached altitudes of 11.2 and 15.5 km, respectively. A comparison of the recorded electroscope reading at the 5 km level during ascent with the reading at the same level during descent shows that the average discharge rate of the electroscopes while above the 5 km level was about three times their discharge rates at the surface of the earth, and corresponded to an average rate of production of ions of 46.2 ions per cc per sec. This is only 25 percent of the value to be expected from the observations of Hess and of Kolhörster and constitutes definite proof that there exists no penetrating radiation of cosmic origin having an absorption coefficient as large as 0.57 per meter of water.

It was as early as 1903 that the Canadian physicists McLennan and Burton[1] and Rutherford and Cooke[2] noticed that the rate of leakage of an electric charge from an electroscope within an air-tight metal chamber could be reduced as much as 30 percent by enclosing the chamber within a completely encircling shield or box with walls several centimeters thick. This meant that the loss of charge of the enclosed electroscope was not due to causes inside the electroscope but must rather be due to some highly penetrating rays, like the gamma rays of radium, which could pass through metal walls as much as a centimeter thick and ionize the gas inside.

In view of this property of passing through relatively thick metal walls in measurable quantity, the radiation thus investigated was called the "penetrating radiation" of the atmosphere, and was at first quite naturally attributed to radioactive materials in the earth or air, and this is in fact the origin of the greater part of it. But in 1910 and 1911 it was found that it did not decrease as rapidly with altitude as it should upon this hypothesis. The first significant report upon this point was made by the Swiss physicist, Gockel,[3] who took an enclosed electroscope up in a balloon with him to a height of 4500 meters and reported that he found the "penetrating radiation" about as large at this altitude as at the earth's surface, and this despite the fact that according to Eve's[4] calculation it ought to have fallen to half its surface value in going up 250 feet.

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[1] McLennan and Burton, Phys. Rev. **16,** p. 184 (1903).

[2] Rutherford and Cooke, Phys. Rev. **16,** 183 (1903).

In 1911, 1912, 1913, and 1914 two other European physicists, Hess[5] an Austrian, and Kolhörster,[6] a German, repeated these balloon-measurements of Gockel's, the latter going up to a height of 9 km, or 5.6 miles, and reported that they found this radiation decreasing a trifle for the first kilometer or so and then increasing until it reached a value at 9 km, according to Kolhörster's measurements, seven times as great as at the surface. This seemed to indicate that the penetrating rays came from outside the earth, and were therefore of some sort of cosmic origin. If so it was computed[7] that in order to fit the Hess and Kolhörster data, the rays had to have an absorption coefficient of .57 per meter of water and an ionizing power within a closed vessel sent to the top of our atmosphere of at least 500 ions per cc per sec., in place of the 10 or 12 ions found in ordinary electroscopes at the surface.

The following table gives a summary of all the Hess-Kolhörster data which in 1914 stimulated the interest of one of us in the problem and furnished the basis for the computations with the aid of which our sounding-balloon apparatus was designed. The earliest of these designs was made in 1915–16, but was not completed because the war put a stop

TABLE I

Hess

Altitude in Meters	Ions per cc per sec. in excess of ground value Instrument No. 1	Instrument No. 2
0 – 200	− 0.9	− 0.7
200 – 500	− 0.8	− 1.4
500 – 1000	− 0.7	− 1.5
1000 – 2000	− 0.4	+ 0.3
2000 – 3000	+ 1.0	+ 1.5
3000 – 4000	+ 3.5	+ 4.7
4000 – 5200	+18.1	+15.4

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[3] Gockel, Phys. Zeits. **11,** 280 (1910).

[4] Eve, Phil. Mag. **21,** 26 (1911).

[5] Hess, Phys. Zeits. **12,** 998 (1911), and **13,** 1084 (1912).

[6] Kolhörster, Phys. Zeits. **14,** 1153 (1913), and Verh. d. Deut. Phys. Ges. (July 30, 1914).

[7] H. von Schweidler, Elster u Geitel Festschrift, p. 411, 1915.

Kolhörster

Flight 1		Flight 2		Flight 3		Flight 4	
Alt.	Ions	Alt.	Ions	Alt.	Ions	Alt.	Ions
310	− 1.2	500	− 2.0	1090	− 1.2	1000	− 1.5
760	− 1.3	600	− 1.4	2130	+ 2.1	2000	+ 1.2
1650	+ 0.8	1000	− 2.1	3550	+ 7.0	3000	+ 4.3
2110	+ 1.3	1400	− 1.7	4700	+14.5	4000	+ 9.3
2400	+ 3.1	1500	− 0.8	5600	+27.5	5000	+17.2
2600	+ 4.3	2400	+ 3.1	6200	+29.3	6000	+28.7
3000	+ 7.5	3300	+ 4.5			7000	+44.2
3400	+ 8.9	4000	+ 6.7			8000	+61.3
3500	+11.1					9000	+80.4

to further activity in this direction. Upon the cessation of the war about two years were spent in trying to have built the right kind of sounding-balloons. In the winter of 1921–22 with the aid of Mr. Julius Pearson we designed and had constructed in the Norman Bridge Laboratory of Physics four little recording electroscopes. These we took to Kelly Field near San Antonio, Texas, in the spring of 1922, for the purpose of attempting to get them as near as possible to the top of the atmosphere in order to obtain a crucial test as to whether there is such a cosmic radiation as the Hess-Kolhörster data seemed to require.

These electroscopes were made of steel 0.3 mm thick, and were designed to support an internal pressure of 10 atmospheres, our intention being to increase, if necessary, the rate of leak by using air at high pressure. Actually, however, the two successful flights were made at atmospheric pressure, since Kolhörster's data indicated that there existed a penetrating radiation of such intensity as completely to discharge the electroscope during the flight if the ten atmospheres pressure were used. In addition all the electroscopes carried photographic films and the necessary driving mechanism for obtaining a continuous record during the ascent and descent (1) of the divergence of the electroscope fibres, (2) of the temperature and (3) of the barometric pressure. The total weight of each with all its contents was but 190 grams, or about 7 ounces.

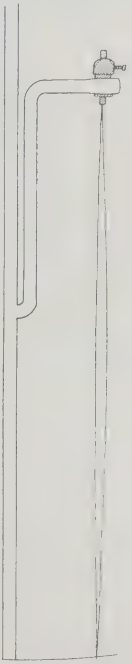

Fig. 1.

Plate 1a shows a photograph of one of these instruments ready for flight, and placed beside it a six-inch (15 cm) rule. Plate 1b shows the inner mechanism. The electroscope consists of two sputtered quartz fibres such as are used in a Wulf electroscope, the deflection of which was produced by charging with a 300 volt battery through the movable charging-rod *C*. To make them as free from temperature effects as possible, all the supports were of quartz and of the shape shown in Fig. 1.

The lower spring was a single quartz fibre, having suitable elastic properties, rigidly attached at one end only. These supports are all inside the metal shield *M*, Plate 1b, provided to eliminate the effect of static charges on the quartz. A shadow image (diffraction pattern) of the fibres produced by the light from the sky passing through an exceedingly fine vertical slit S_1 carried by the slit holder shown at the left of the rule in Plate 1a fell upon the photographic film through a wide horizontal slit S_2 on the opposite side of the cylinder. The thermometer *T* was a small coil of duo-metal carrying a minute pointer *P* which moved up and down a vertical slit *N* behind which the photographic film was moving, the whole being illuminated by skylight entering through a fine horizontal slit *H* in the cap which fitted, light tight, over the thermometer and barometer chamber. The barometer *B* is a small, closed-arm manometer, the top of the liquid surface in one arm of which is also registered on the photographic film by skylight entering through *H*. The two circular films and the black paper separating them were fastened on the carrier *F* which was directly connected to the main spring of the small watch *W*.

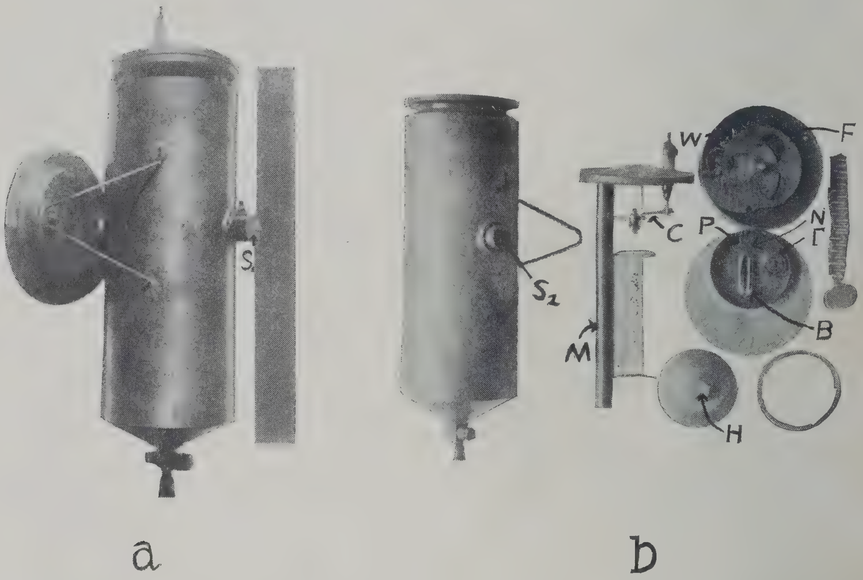

Plate 1. a. The complete recording instrument ready for flight. A 6-inch (15 cm) rule is shown beside it for comparison.
b. The inner mechanism.

Each of these electroscopes was carried up by two balloons eighteen inches across when deflated and weighing about 300 grams apiece. These balloons were specially made from our specifications by the Sterling

Rubber Company of Guelph, Canada. They were inflated with hydrogen to a buoyancy of 550 grams each (diameter about 95 cm) and rose at a rate of 130 meters per minute when carrying between them a total load of 220 grams (electroscope, cord, directions for return and so forth).

The rates of ascent were measured by the two-theodolite method, Lieutenant McNeal was especially sent from Washington to Kelly Field by Major William R. Blair of the U. S. Signal Corps to assist us in these experiments by making these two-theodolite altitude measurements.

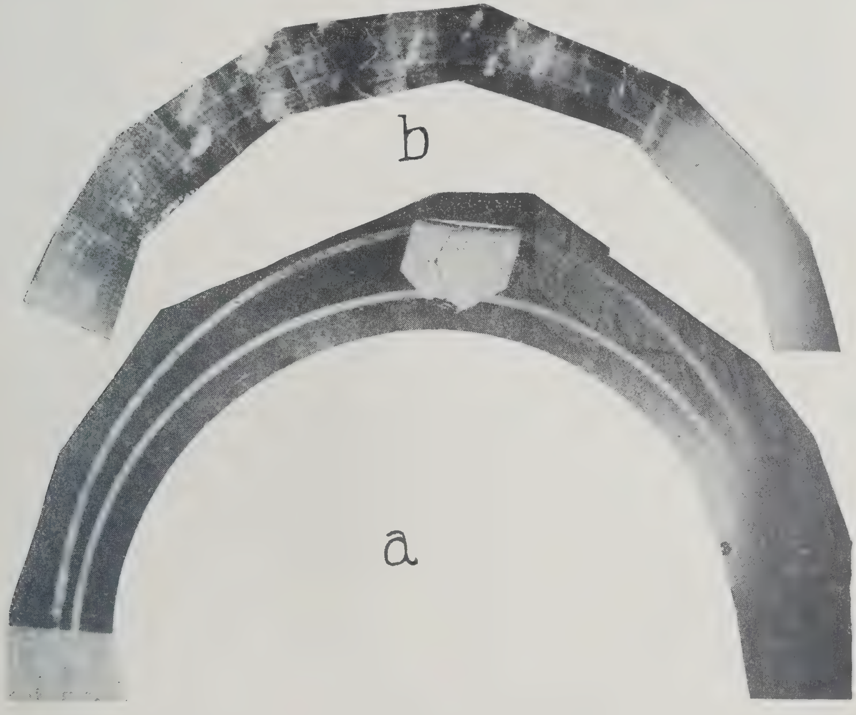

Plate 2. a. Reproduction of the photographic film giving the temperature record of the 15.5 km flight.

b. Reproduction of the photographic film giving the divergence of the electroscope fibers during the 15.5 km flight.

The purpose of sending up two balloons with each instrument is not merely to gain additional buoyancy but to enable one of them to bring the instrument safely to earth after the other has burst and also to serve, after the return to earth, to attract attention and increase the likelihood of the return of the instrument to the sender as per instructions attached to it.

We succeeded in making four flights and had three instruments returned, two of which had reached the altitudes of 11.2 and 15.5 kilometers respectively. They were returned from distances about eighty miles away from the starting point.

Plate 2a is a reproduction of the photographic film giving the temperature record of the 15.5 kilometer flight. The film was driven at the rate of 48° to the hour, the total time of flight as shown by this film was three hours and eleven minutes. This was accurately determined by plotting as in Fig. 2 the slopes of the time-temperature curve going up and coming down. The point of intersection of these two slopes gives the exact time at which one of the balloons burst and the descent began. The temperature at this time was in this case $-60°C$, as measured by the divergence of the two traces, a divergence read with a microscope and accurately calibrated by preceding laboratory tests down to $-77°C$. The horizontal edge on the left side of the blackened portion of the film gives the instant at which the driving mechanism was started just before the beginning of the flight. In this particular flight the apparatus reached the earth just after sunset and for this reason the thermometer record vanishes before the temperature has quite returned to the initial value, but the rate of descent is altogether uniform so that no uncertainty is thereby introduced into the time of flight. The time of ascent was in this case 115 minutes and that of descent 76, the total being 191 minutes. The

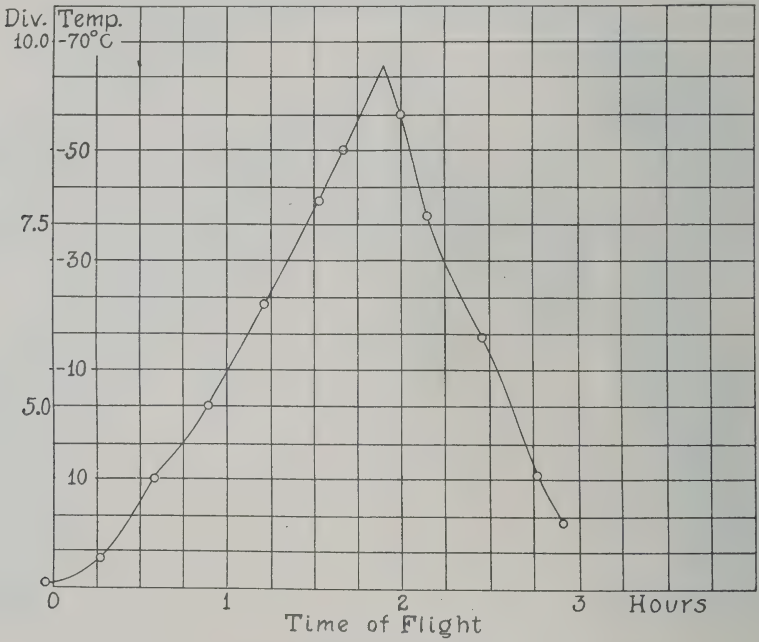

Fig. 2. The time-temperature curve for one flight.

relative times of ascent and descent are determined accurately from the ratio of the slopes of the ascending and descending portions of the temperature curve.

Plate 2b is a reproduction of the photographic record of the divergence of the electroscope fibres during the three hours and eleven minutes of this flight. It will be seen that the two lines representing the shadows of the fibres on the film lend themselves very well to accurate microscopic measurement. Indeed, there was a very sharp diffraction edge on each side of each line which made the setting particularly exact. On account of the fact that we were interested only in discharge rates at high altitudes we used for our computation of these discharge rates the initial measurements of the deflection of the fibres when the instrument had reached an altitude of 5 kilometers on the ascent, and final measurements of the fibre-deflection when it had reached again the same altitude of 5 kilometers on the descent. Since the temperature of the instrument is the same at a given altitude while going up as while coming down, our discharge rates are thus made entirely independent of the influence of temperature upon the elastic properties of the fibres and supports—a matter that we have found to be of greatest importance.

Fig. 3 contains the graphical representation of all of the electroscope readings as well as the time-altitude determinations, abscissas being time in hours and the scale of ordinates to the right, altitude in kilometers, while the scale of ordinates to the left represents fibre-deflections. The straight sloping lines meeting at the top represent the constant rates of ascent and of descent, the first of which are obtained from direct theodolite measurements.

The line *G* at the top sloping gently downward is the rate of discharge in scale divisions while the instrument was at the surface. This discharge rate is very accurate since it was taken over a discharge period of twenty-four hours. It will be seen that the straight line *F* connecting the two groups of points representing measurements at the two 5 kilometer altitudes has a slope corresponding to a mean discharge rate three times that found at the earth's surface. *This shows quite unambiguously, in agreement with the findings of Gockel, Hess, and Kolhörster, that the discharge rates at high altitudes are larger than those found at the surface.* Quantitatively, however, there is complete disagreement between the Hess-Kolhörster data and our own, the total loss of charge of our electroscope in the two hours spent between the altitudes of 5 km and 15.5 km having been but about 25 percent of that computed from the Hess-Kolhörster curve which is represented by the curved line *K* of Fig. 3. The data plotted in Fig. 3 also shows very beautifully that, despite the extraordinary precautions herein taken to make an electroscope whose readings would be independent of temperature, there was nevertheless a marked temperature effect. Thus Fig. 3 shows that the apparent deflection reaches a minimum when the temperature is a minimum and then rises again as the instrument warms up in the descent. *Our results are entirely free from these temperature effects since our initial and final readings are taken under the same temperature conditions.*

The mean rate of discharge in the ascent from 5 km to 15.5 km and the descent again to 5 km of this electroscope was 46.2 ions per cc per sec. The average rate of discharge of the same electroscope at the surface was 15.4 ions per cc per sec., so that the mean rate of discharge at these very high altitudes here attained was but three times the surface rate, in contrast with the sevenfold rate shown by the data in Table 1 at the lower altitude of 9 km.

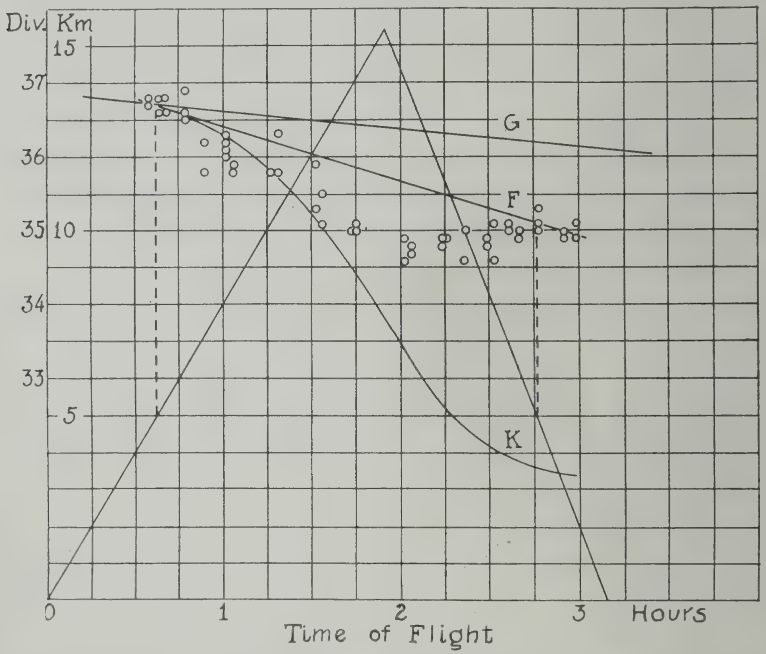

Fig. 3. Electroscope readings and altitude determinations as functions of the time.

Another flight which reached an altitude of 11.4 km also yielded a total loss of charge not more than 25 percent of that found by the European observers, though some temperature changes rendered its evidence much less reliable than that of the 15.5 km flight.

The results then of the whole Kelly Field work constitute definite proof that there exists no radiation of cosmic origin having such characteristics as we had assumed. They show that the ionization increased much less rapidly with altitude than would be the case if it were due to rays from outside the earth having an absorption coefficient of .57 per meter of water.

Taken in conjunction, however, with experiments on absorption coefficients to be reported in the succeeding articles II and III—experiments which present unambiguous evidence for the existence of a cosmic radiation of extraordinary penetrating power, μ calculated as above being as low as .18 per meter of water, these experiments at very high altitudes have important bearings upon the distribution in wave-length of these hard rays as they enter the atmosphere.

Norman Bridge Laboratory of Physics,
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Pasadena, California,
December 24, 1925.

A CORRESPONDENCE PRINCIPLE IN THE COMPTON EFFECT*

By G. Breit

Abstract

Correspondence theorem for frequencies.—It is well known that the frequency emitted by a hydrogen atom as it falls from one of its quantized states to another may be expressed as a mean value of the frequency of motion of the electron (or overtone thereof) when averaged in the proper manner over orbits intermediate between the initial and final states. In the present paper it is *proved* that, similarly, *the Compton shift is a properly taken mean of the classical Doppler shift.* The quantum frequency actually scattered is thus a properly taken average of the frequency which would be scattered on the classical theory as the electron is accelerated from its state of rest to its final recoil condition.

Correspondence principle for intensities.—In like manner, the amount of light scattered in various directions may be determined if it is *assumed* that the intensity in the quantum theory equals a proper average of the intensities scattered according to the classical theory. A comparison is made with observed data on the scattering of γ-rays.

The characteristic feature of the present paper is that *the corresponding classical electron is assumed to have the same direction of motion as the scattered quantum,* whereas an actual classical electron would from symmetry recoil straight forward in the direction of the incident beam, as in Compton's and Woo's theories of intensities. This new point of view eliminates the difficulty of a constant correction-factor which has been encountered by Compton and Woo in their explanation of intensity relations.

1. Introduction

THEORIES giving the dependence of the intensity of scattered radiation upon the angle have been given by Compton, Debye, and Woo. The theory of Debye is in poor agreement with experiment. The theories of Compton and Woo agree with experiment except for the occurrence of a factor $1+2\Lambda/\lambda_0$ which must be omitted in order to satisfy the experimental facts. The theory of Compton and Woo postulates that the intensity of the scattered radiation may be obtained by considering the classical scattering by an electron having the velocity $c\Lambda/(\Lambda+\lambda_0)$, where c is the velocity of light, λ_0 the wave-length of the incident radiation, and $\Lambda = h/m_0c$, h being Planck's constant and m_0 the rest mass of the electron. The reason for this assumption as given by Compton is that such an electron scatters radiation of the right frequency and that, therefore, it may also be expected to scatter it with the right intensity.

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* Presented at the Kansas City meeting of the American Physical Society, Dec. 1925.

A priori there is no objection to this reasoning. However, the calculations of the above authors show that their picture is not altogether satisfactory. The factor by which their result must be divided is just such as to give the classical intensity in the direction of the incident radiation. This fact in itself suggests another point of view.

The emitting atom and the scattering electron may be conceived as one complex atom. The scattering process is the emission process of that atom. In its initial state the electron is at rest, and in the final state the electron is in motion. According to Bohr's correspondence principle we should expect that both *the frequency of the emitted radiation and its intensity are given by proper averages of the corresponding quantities between the initial and final states.* It is clear without calculation that such a point of view leads us to expect the same intensity in the direction of incident radiation as is demanded by the classical theory, because in this case there is no recoil of the electron. We first show that the frequency actually scattered is a properly taken average of the frequency scattered classically in the initial and final states of the scattering electron. We then calculate the intensity of scattered radiation in the initial and final states and we show that a proper mean of these values is in agreement with experiment. Even though we apparently adhere in this to the prescriptions of the correspondence principle, we cannot altogether put this problem on the same footing as the application of the correspondence principle to the atomic frequency theorem of Bohr or to the selection rules. To do this it would be necessary to obtain a description of the possible atomic states by means of phase integrals.

2. Correspondence Theorem for Frequencies

The quantum theory of the Compton effect is governed by the relations

$$\begin{aligned} \frac{m_0 v}{\sqrt{1-\beta^2}} \cos\varphi + \frac{h\nu_\theta}{c}\cos\theta &= \frac{h\nu_0}{c} \\ -\frac{m_0 v}{\sqrt{1-\beta^2}} \sin\varphi + \frac{h\nu_\theta}{c}\sin\theta &= 0 \qquad \text{(I)} \\ m_0 c^2\left(\frac{1}{\sqrt{1-\beta^2}}-1\right) + h\nu_\theta &= h\nu_0 \end{aligned}$$

where the electron is supposed to be at rest before scattering. In these relations $h\nu_0$ and $h\nu_\theta$ are the magnitudes of the original and scattered quanta, respectively; θ, the angle between their directions; φ, the angle between the velocity v of the electron after scattering and the incident radiation; and β is v/c. As is known, when these equations are solved for ν_θ one finds

$$\nu_\theta = \frac{\nu_0}{1+\frac{\nu_0}{N}(1-\cos\theta)} \tag{II}$$

where

$$N = \frac{m_0 c^2}{h}. \tag{II'}$$

In order to determine the frequency which would be scattered by the electron in its final recoil state we must consider first of all what the incident frequency appears to be to an observer on the moving electron. We must next compute how the scattered radiation is transformed to the stationary frame of reference. The system of the recoil electron we refer to as K' and to that of the stationary one we refer as K. In the equations of the Lorentz transformation we take the X axis along the direction of recoil. The fundamental relation is

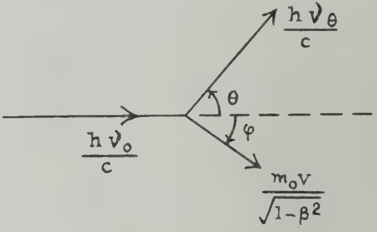

Fig. 1.

$$\frac{\nu}{\nu'} = \frac{1+\beta\cos\psi'}{\sqrt{1-\beta^2}} = \frac{\sqrt{1-\beta^2}}{1-\beta\cos\psi} \tag{III}$$

where Ψ is the angle with the X axis referred to K, Ψ' is the same angle referred to K' and ν, ν' are the frequencies of the radiation referred to K, K' respectively. We have, therefore, for the frequency scattered by the recoil electron on the basis of classical relativity

$$\frac{\nu_{\theta c}}{\nu_0} = \frac{1-\beta\cos\varphi}{1-\beta\cos(\theta+\varphi)} \tag{1}$$

It follows from (1) that

$$\beta\cos(\theta+\varphi) = \frac{\nu_0\cos\theta-\nu_\theta}{N+\nu_0-\nu_\theta} \tag{2}$$

$$\beta\cos\varphi = \frac{\nu_0-\nu_\theta\cos\theta}{N+\nu_0-\nu_\theta} \tag{3}$$

Whence using (II) we have

$$\frac{\nu_{\theta c}}{\nu_0}=\frac{N-\nu_\theta(1-\cos\theta)}{N+\nu_0(1-\cos\theta)}=\frac{1}{\left(1+\frac{\nu_0}{N}(1-\cos\theta)\right)^2}=\left(\frac{\nu_\theta}{\nu_0}\right)^2 \tag{4}$$

This means that

$$\log\nu_\theta=\frac{1}{2}\left[\log\nu_0+\log\nu_{\theta c}\right] \tag{5}$$

In other words the logarithm of the scattered frequency is the arithmetic mean of the frequency which would be scattered in the initial and in the final states on the basis of the classical theory. If $(\nu_\theta-\nu_0)/\nu_0<<1$ we also have approximately $\nu_\theta=\frac{1}{2}(\nu_0+\nu_{\theta c})$ as may be shown by a simple consideration of the vector diagram.

It is hardly necessary to point out that Eq. (5) is not altogether analogous to Bohr's Correspondence Theorem, for in that theorem attention is paid to the classical frequency in every intermediate step. In (5), however, we only use the mean of the end values of the classical frequency. It is perhaps dangerous to try to use a method entirely analogous to Bohr's because the Compton shift does not exist on the classical theory.

In a purely speculative manner, however, we may try to look at the problem from the following point of view. Since the quantum emission process is entirely unidirectional, the "corresponding" classical picture we take to be also entirely unidirectional. The classical plane wave is incident on the scattering electron and gradually imparts to it its final momentum. At any intermediate stage in this scattering process the electron is executing a recoil motion which, however, is smaller than the final one. We shall attempt to justify presently the assumption that the classically scattered frequency must be averaged by regarding h in (4) as a variable having a range between 0 and 6.55×10^{-27}. The weights of equal intervals in this range we consider as equal. Letting

$$a=\frac{1-\cos\theta}{m_0c^2}, \tag{6}$$

the average frequency emitted is according to (5)

$$\bar{\nu}_{cl}=\frac{1}{h}\int_0^h\frac{\nu_0dx}{(1+a\nu_0x)^2}=\frac{\nu_0}{1+a\nu_0h}=\nu_\theta, \tag{7}$$

as is seen from (II). This means that the scattered frequency is a properly taken average of the classically scattered frequency.

The justification for taking the average in the manner indicated by (7) may be seen in the fact that Bohr's correspondence theorem assigns equal weights to equal elements of length on the straight line in n-dimensional space joining (J_1, J_2, ...) to (J_1+n_1h, J_2+n_2h, ...). Considering for simplicity the one-dimensional case, the frequency emitted is $\overline{n(\partial W/\partial J)}$ where W is the energy and where the average is taken between J and $J+nh$, equal weights being attached to all elements dJ. It is clear that equal weights are attached to all intervals corresponding to equal energy intervals as long as W increases uniformly with J. In general W does not increase uniformly with J, this being rigorously the case only for a linear oscillator. The averaging assumption included in (7) means that equal values of ΔW referred to the original emitting atom correspond to equal weights in the scattering mechanism. To this extent we suppose the emitting atom to be equivalent to a linear resonator at a large distance.

We think, therefore, of the emitting atom and the scattering electron as one complex atom. We have shown by means of II, (4), (7) that the frequency ν_0 which is actually scattered is the average of the frequency which would be scattered on the classical theory provided the *energy* extracted from the quantum incident on the electron determines the linear scale for averaging.

3. CORRESPONDENCE PRINCIPLE FOR INTENSITIES

We may now pass on to the intensity relations. We need first of all to know what intensity the classical theory would give for the radiation scattered in the final recoil state. We adopt as a criterion the intensity scattered per unit solid angle in the direction θ of the actually scattered radiation. We shall simplify the calculation by showing that in the frame of reference of the recoil electron the incident and recoil quanta make with each other the same angle θ as in the frame of reference of the electron before scattering. This fact, as well as others useful in connection with the present problem, can be obtained most simply by using Pauli's very elegant treatment of the interaction between quanta and electrons.[1] Pauli denotes the energy of the quantum by E, its momentum by Γ, the energy of the electron by U and its momentum by G. He then shows that if a frame of reference be chosen such that in it Γ and G are equal and opposite before impact, then after impact Γ and G are equal and opposite, and, further, the new values of Γ and G as well as the new values of E and U are all equal respectively to their old values. The only change in that frame which occurs at collision is a change in the direction of all the vectors without change in absolute magnitude. It is clear from this fact and the symmetry of Fig. 2 that a Lorentz transformation to a frame of reference moving with velocity v along G leads to the same result for the angle between Γ and Γ' as the Lorentz transformation to a frame moving with the same velocity v along G'. This proves that in the frame of the recoiling electron the angle between the incident and the reflected quantum is the same angle θ as that formed in the frame of the electron before collision.

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[1] W. Pauli, Zeits. f. Physik **18**, 272 (1923).

[2] Laue, Die Relativitätstheorie, Vol. I, p. 124, formula 177; Vieweg, 1921.

It further proves that in the frame of the recoiling electron the reflected quantum has the magnitude $h\nu_0$ and the incident quantum has the magnitude $h\nu_\theta$, while in the frame of the electron before collision the reflected quantum has the magnitude $h\nu_\theta$ and the incident one is $h\nu_0$. (The magnitude of the quantum is the same if referred to the electron before and after collision.)

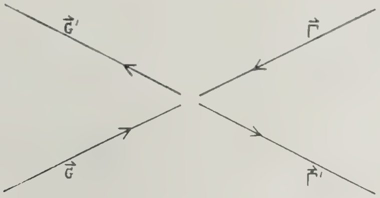

Fig. 2.

Suppose now in K' (the frame of the recoil electron) the amount of energy radiated into the angular domain $d\theta'$, $d\varphi'$ is

$$f(\theta',\varphi')\sin\theta'\,d\theta'\,d\varphi' \tag{8}$$

then in the stationary frame of reference K this radiation appears to have an energy content greater than the above in the ratio $\nu^2:\nu'^2$ so that an amount of energy

$$\frac{\nu^2}{\nu'^2}f(\theta',\varphi')\sin\theta'\,d\theta'\,d\varphi' \tag{9}$$

is radiated into the corresponding angular domain $d\theta$, $d\varphi$.[2]

Since

$$\sin\theta'\,d\theta'\,d\varphi'=\frac{\nu^2}{\nu'^2}\sin\theta\,d\theta\,d\varphi \tag{10}$$

we have an amount of energy

$$\left(\frac{\nu}{\nu'}\right)^4 f(\theta',\varphi') \tag{11}$$

per unit solid angle in K. In this formula it is important to remember that ν/ν' refers to one particular direction of radiation, namely, that of the recoiling quantum. Therefore, here we must write

$$\frac{\nu}{\nu'}=\frac{\nu_\theta}{\nu_0} \tag{12}$$

making the energy distribution

$$\left(\frac{\nu_\theta}{\nu_0}\right)^4 f(\theta',\varphi') \tag{13}$$

The expression for $f(\theta', \varphi')$ is obtained by considering what becomes of the incident radiation when it is transformed to the frame of the recoil electron. If the intensity of this radiation in K is I_0 and if in K' it is I_0' the value of $f(\theta', \varphi')$ is given by the Thomson expression

$$f(\theta',\phi')=CI_0'\frac{1+\cos^2\theta}{2} \tag{14}$$

where

$$C=\frac{e^4}{c^4m^2}$$

because the angle between the scattered and incident radiation we showed to be θ in K'. Further

$$I_0'=\left(\frac{\hat{\nu}'}{\hat{\nu}}\right)^2 I_0 \tag{15}$$

where $\hat{\nu}'/\hat{\nu}$ is the quotient of the frequencies computed by the Lorentz transformation for a ray in the direction of the incident quantum. Since in K this quantum is $h\nu_0$ and in K' it is $h\nu_\theta$

$$\frac{\hat{\nu}'}{\hat{\nu}}=\frac{\nu_\theta}{\nu_0} \tag{16}$$

and the amount of energy scattered per unit time by the recoil electron from a beam of radiation of intensity I_0 is

$$\mathscr{I}_\theta=CI_0\left(\frac{\nu_\theta}{\nu_0}\right)^6\frac{1+\cos^2\theta}{2}=\frac{CI_0}{\left[1+\frac{\nu_0}{N}(1-\cos\theta)\right]^6}\,\frac{1+\cos^2\theta}{2} \tag{17}$$

where use has been made of II. We write this also as

$$\mathscr{I}_\theta = I_{\theta c}\left[1+\frac{\nu_0}{N}(1-\cos\theta)\right]^{-6} \tag{18}$$

where $I_{\theta c}$ is the classical expression of J. J. Thomson, which does not take into account the Compton shift.

The above expression $\mathscr{I}$ represents the rate at which energy is emitted by the electron during the scattering process. It does not represent, however, the amount of energy scattered in a given direction because if a train of finite length is incident the length of the train reemitted in the direction θ is not necessarily the same. Since the number of waves in the incident and the scattered rays is the same, the ratio of the two lengths is the same as the ratio of the wave-lengths as measured in K or the inverse ratio of the frequencies. Hence the amount of energy scattered is, using (4),

$$I_\theta = \frac{\nu_0}{\nu_{\theta c}}\mathscr{I}_\theta = \left(\frac{\nu_0}{\nu_\theta}\right)^2 \mathscr{I}_\theta \, . \tag{19}$$

We have, therefore, substituting (18),

$$I_\theta = I_{\theta c}\left[1+\frac{\nu_0}{N}(1-\cos\theta)\right]^{-4} . \tag{20}$$

Expression (20) represents the average rate at which energy is scattered by the electron if a number of trains of waves are incident, while (18) gives the rate of scattering during the incidence of one of the trains. Which of these expressions one must use depends upon the application. The important fact is that both I_θ and $\mathscr{I}_\theta$ are less than $I_{\theta c}[1+(\nu_0/N)(1-\cos\theta)]^{-3}$ and that the latter expression represents satisfactorily the experimental results. Expression (20) appears to be the correct one to use if the total amount of energy scattered is taken as the criterion. From that point of view very much more weight should be attached to the properties of the recoil electron than to those of the stationary one in calculations of intensity because the difference between $(1+y)^{-3}$ and $(1+y)^{-4}$ is smaller than between 1 and $(1+y)^{-3}$. Thus for small y

$$1-(1+y)^{-3} \cong 3y \text{ and } (1+y)^{-3}-(1+y)^{-4} \cong y$$

while for large y

$$1-(1+y)^{-3} \cong 1 \text{ and } (1+y)^{-3}-(1+y)^{-4} \cong 0$$

In justification of using expression (18), however, one may say that it deals with the stationary rate at which energy is scattered while a plane wave is continuously incident on the recoiling electron. Therefore, if the emitting atom and the recoiling electron are considered as a unit which is constantly radiating, expression (18) is the right one to use. It is a curious fact that the transition from (18) to the empirical formula

$$\bar{I}_\theta = I_{\theta c}\left[1+\frac{\nu_0}{N}(1-\cos\theta)\right]^{-3} \tag{21}$$

may be thought of as very analogous to the transition from $\nu_{\theta c}$ to ν_θ represented by (4). We may say in fact that (21) is obtained from (18) by using the same intermediate value of the averaging parameter x (see Eq. 7) as that which makes $\nu_{\theta c}$ go into ν_θ. In fact, this value is such that

$$\frac{1}{(1+a\nu_0 x)^2} = \frac{1}{1+a\nu_0 h}$$

and therefore

$$\frac{I_{\theta c}}{(1+a\nu_0 x)^6} = \frac{I_{\theta c}}{(1+a\nu_0 h)^3}$$

The meaning of this method of averaging is that the radiating ability of the atomic system is considered in such an intermediate stage that the classically computed frequency is the actual emitted frequency. It is of course known from the phenomena of dispersion that the reaction of an atomic system to a light wave depends on the properties of "virtual oscillators," and that the frequency of these oscillators is the quantum transition frequency. We attempt above to interpret this as meaning that approximately at least this is due to the action of an intermediate atomic system which is determined by that stage of the transition in which Bohr's corresponding frequency is equal to the emitted frequency.

It would be desirable, of course, to compare this method of averaging with others also in other cases. In view of the uncertainty of the atomic models, we cannot make a definite statement. However, it seems that the method used here is not worse than the customary ways of averaging and that it allows one to understand why in Lande's g-formula $j(j+1)$ takes place of j^2. A reason for this may be seen in the fact that different values of j correspond to different k's in the relativistic separation formula which is obeyed empirically with j substituted for k. This means that the dependence of the energy level on j is given by a term of the form A/n^3j (A a constant) and therefore the "corresponding" frequency is such that the value of j which corresponds to it is given by

$$\frac{1}{{}_c^{2}}=\frac{1}{j}-\frac{1}{j+1}$$

This means that $j_c^2=j(j+1)$. Our assumption is here that the interaction between parts of an atom is not determined by the actual state of the atom but by a state intermediate between the state and a neighboring one, this intermediate state being chosen in such a way that the orbital frequency is equal to the frequency which would be emitted in the transition between the two states.

4. Comparison with Experiment

A comparison with experiment cannot be carried out satisfactorily at present on account of the scarcity of experimental material. The measurements on the Compton effect for x-rays are not covered by the above theory on account of the influence of atomic structure on the phenomenon of scattering. This question is treated in various papers by Jauncey.[3] We must rely, therefore, on the measurements of A. H. Compton[4] in the range of hard γ-rays. In these the wave-length of the scattered γ-rays has not been determined, and it is not known whether all of the scattered radiation was modified. Compton determined intensities of scattering in various directions relatively to scattering at 90°. He also found that $I_{90°}/I_0=0.037$. In the adjoining table the first column gives the angle of scattering, the second the average of Compton's experimental relative values, the third these values multiplied by 0.037, and the fourth values computed from our formula (21). The numbers in the fourth column are higher than those in the third. The fifth column gives ratios of numbers in the fourth to those in the third. The average of these is 1.3. It is striking that this is the ratio of 0.048 to 0.037. If, therefore, on account of a systematic error Compton's determination for 90° should be in error to that degree, formula (21) may be considered as representing experiments satisfactorily.

Table II

θ	Average Relative Value	0.037χ Av. Rel. Value	Theoret. $I_{\theta c}(\frac{\nu_\theta^3}{\nu_0})$	$\frac{\text{Theor.}}{\text{Exp.}}$
30°	10.5	0.389	0.555	1.4
45	6.87	0.254	0.305	1.2
60	4.3	0.159	0.156	1.0
75	1.97	0.073	0.080	1.1
90	1.0	0.037	0.0476	1.3
120	0.7	0.0259	0.0288	1.1
135	0.45	0.0166	0.0267	1.6
150	0.47	0.0172	0.0260	1.5

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[3] Jauncey, Phys. Rev. **25,** 314, 723 (1925); Phil. Mag. **49,** 427 (1925).

[4] Compton, Phil. Mag. **46,** 897 (1923).

It must be emphasized, however, that a definite conclusion may not be drawn at present because it is not known whether the unmodified radiation was entirely absent in Compton's experiments. Even a small amount of it would change the interpretation of the experiments because its dependence on the angle of scattering is very different from that given by (21). In Fig. 3 the J. J. Thomson formula is represented by $I_{\theta c}$, our (21) by $I_{\theta c}(\nu_\theta/\nu_0)^3$ and Compton's experimental values by the small circles.

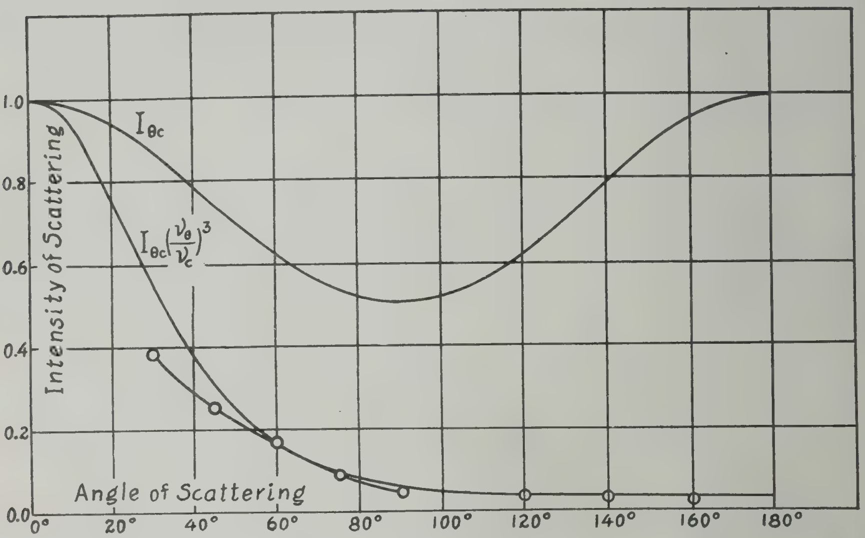

Fig. 3.

Department of Terrestrial Magnetism,
Carnegie Institution of Washington,
Washington, D. C.
January 26, 1926.

APRIL, 1926 PHYSICAL REVIEW VOLUME 27

AN EFFECT OF TEMPERATURE ON X-RAY ABSORPTION

By H. S. Read

Abstract

The effect of temperature on the average atomic absorption coefficients for x-rays.—The variation with temperature of the absorption by sheets of Al, Cu, Fe, Ni, Ag, and Pb of the total x-radiation from a tungsten x-ray tube operated at 50 kv has been studied. The measurements were made by balancing the ionization currents produced by two x-ray beams from the same tube, one of which passed through the absorber. After proper corrections are made for changes in the density of the absorber and of the air in the path of the beam, there remains a residual effect indicating a true variation of the atomic absorption coefficient with temperature. The results indicate that for all absorbers used the average atomic absorption coefficients for the total x-radiation from the tungsten target increased nearly linearly with the temperature by about 0.2 percent per 100°C up to temperatures near the melting point of the absorber. The work is being continued to determine the magnitude of the effect at different wave-lengths.

THE statement has been made,[1,2,3] and is generally accepted, that heating a crystal affects measurably its ability to reflect x-rays. Also it has been stated[4] that x-ray absorption is independent of all physical conditions, and specifically, independent of temperature. The critical analysis of x-ray phenomena show such close relations between transmission, reflection, scattering, and absorption that they appear to be consequences of one or two more fundamental phenomena. The object of the present work was to search for an effect of temperature on x-ray absorption by the metals, Al, Fe, Ni, Cu, Ag, and Pb.

A small temperature effect has been found and measured. Although this preliminary work does not give the accurate value of the small effect, it shows the existence of the temperature effect and the experiments are being continued to determine the value for the different wave-lengths.

Method and Apparatus

A balance method of measurement was used. Two beams from one Coolidge tungsten x-ray tube (Fig. 1) were isolated by four pairs of lead slits and a Bumstead electroscope indicated their balance in two ionization chambers containing methyl bromide. An absorber in one beam was

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[1] W. H. and W. L. Bragg, X-rays and Crystal Structure, 1st ed., pp. 190, 196.

[2] C. G. Darwin, Phil. Mag. **27,** 325 (1914).

[3] P. Debye, Ann. d. Physik **43,** 49 (1914); Vehr. d. D. Phys. Ges. **15,** 678, 738, 857 (1913).

[4] W. H. and W. L. Bragg, X-rays and Crystal Structure, 1st ed., p. 46.

heated by raising up an electric furnace with a narrow slot for the absorber holder. The furnace was 20 cm long, 8 cm inside diameter, and to prevent air currents was closed at the ends by Al sheet .001 cm thick. After raising the furnace the balance was found to be destroyed and the small amount that the adjustable slit in the other beam was changed in order to regain a balance, was recorded. All records and computations were made in terms of the adjustable slit width. Seven or nine trials, alternately hot and cold, were made and the difference between the averages computed. This difference was the uncorrected measure of the temperature effect.

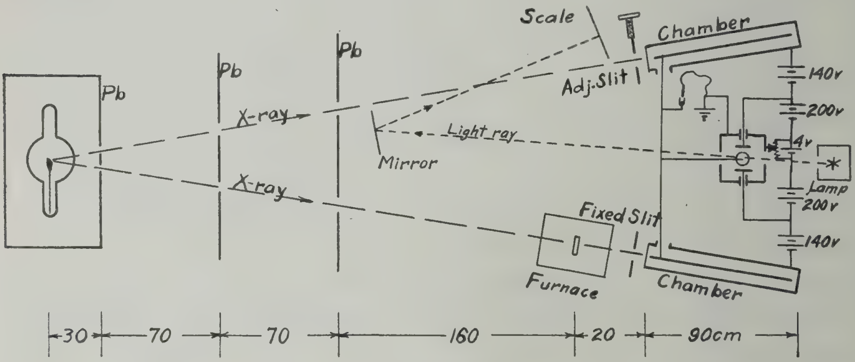

Fig. 1. Arrangement of apparatus.

Six 100 ampere-hour storage batteries were soldered together for a 12 volt source for the tube filament. Over one hour was allowed for the battery to approach a constant discharge current. After that time the tube electron current decreased very steadily at a rate of nearly 0.2 milliamperes per hour. A source of alternating current was obtained by running a compound wound rotary converter on a Terrill regulated d.c. generator. Voltage fluctuations larger than one percent would have been detected on the voltmeter.

The steadiness of operation is measured by the facts that the adjustable slit could be set to 1.0×10^{-4} inch, and when set the electroscope deflection did not change over 1 mm in 10 seconds. However, some unknown cause gave variations as large as 30×10^{-4} inch from day to day. The total absorption of the metals used was equivalent to 6000 to 9000×10^{-4} inch and the temperature effect was from 0 to 200×10^{-4} inch. The maximum slit opening was 1.2400 inch.

An improved Bumstead electroscope was used to indicate the balance between the ionization currents in the two chambers. The sensitivity used was about 150 mm per volt of leaf potential. The possible greater sensitivity[5] would not have increased the accuracy proportionately because errors in single slit settings were smaller than other errors.

A correction for the smaller density of hot air in the x-ray path and for the Al furnace windows was made by measuring the effect of raising the furnace up around the empty holder while the absorber was across the x-ray beam but beyond the furnace. This was done for each absorber at each temperature used and the correction obtained was appropriate for the particular x-rays transmitted through the sample and for the particular furnace temperature. Since the order of position of successive, relatively thin absorbers does not affect much the total absorption, the different location of the absorber for the air correction observations caused no error.

Switching on and off the full load current in the furnace did not give any observable unbalance and consequently it was assumed that the fields of the furnace current did not cause any of the effect found.

The temperatures of the absorbers were measured in arbitrary units by a chromel-alumel thermocouple inside and near the wall of the furnace. Later this couple was calibrated in terms of a standardized Pt-Pt Rh couple, one junction of which was placed between two similar layers of the various absorbers.

Effect of Heat Expansion

The measured change of x-rays transmitted was an absorption and a scattering effect. The latter is not easily computed and was not measured. However it probably was smaller than the absorption effect. For example Kaye[6] says that for the copper group the scattered is sometimes less than 1/200 of the total radiation and A. H. Compton[7] shows that scattering of other elements is of the same order of magnitude or less. And, since the absorber in the furnace covered the beam there and had about twice the area of the final slit the scattering into the beam partly compensated scattering out of the beam. No correction was made for scattering or reflection.

A correction was made for the thermal expansion of the absorber, an appreciable part of which expanded out of the path of x-rays. The beam was defined by a fixed slit, the projected area of which, at the absorber was an area B. Let n represent the number of atoms per cc in the cool absorber, x the cool absorber thickness, a and a' the average atomic absorption coefficients for the absorber cool and hot respectively, I_0 the incident intensity, and I the transmitted intensity. For room temperature the transmitted energy is

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[5] K. Cole has recently calibrated a Bumstead electroscope up to 37,000 mm per volt. J. Optical Soc. of America **10,** 99 (Jan. 1925).

[6] Kaye, X-rays, 4th ed., p. 114.

[7] A. H. Compton, National Research Council Bulletin **4,** Part 2, No. 20, p. 5 (1922).

$$W_1 = BI = BI_0 \exp\left[-anx\right] \tag{1}$$

and for the heated absorber is

$$W_2 = BI_0 \exp\left[-a' \frac{n}{(1+g)^3}(1+g)\right] = BI_0 \exp\left[\frac{-a'nx}{(1+g)^2}\right] \tag{2}$$

where $(1+g)$ is the usual thermal expansion coefficient for the absorber, values of which for the temperature ranges used were obtained from tables of Landolt and Bornstein, 5th edition, p. 1228. The percentage increase in transmitted energy due to heating is given by

$$K_c = \frac{W_2 - W_1}{W_1} = \exp\left[anx - \frac{a'nx}{(1+g)^2}\right] - 1\,. \tag{3}$$

Since the largest value of $2g$ used was .0388 and of anx was 1.69 this expression reduces approximately to

$$K_c = (a-a')nx + 2ga'nx \tag{4}$$

TABLE I

Computed results

		20°	190°	320°	475°	630°	880°	1080°
Al	anx	.66						
.102 cm	K_m	.0003	.0062	.0035	.0060	.0085		
thick	K_c	.0000	.0054	.0102	.0195	.0235		
	$K_m - K_c$	0003	.0008	−.0060	−.0135	−.0150		
Fe	anx	.914						
.014 cm	K_m	.0000	.0025	.0043	.0050	.0075	.0134	
	K_c	.0000	.0038	.0073	.0117	.0164	.0254	
	$K_m - K_c$	.0000	−.0013	−.0030	−.0067	−.0089	−.0120	
Ni	anx	1.14						
.008 cm	K_m	.0014	.0023	.0046	.0071	.0106	.0089	.0190
	K_c	.0000	.0053	.0103	.0150	.0214	.0319	.0410
	$K_m - K_c$	.0014	−.0030	−.0057	−.0079	−.0108	−.0408	−.0220
Cu	anx	1.14						
.009 cm	K_m	−.0002	.0024	.0051	.0078	.0068	.0023	
	K_c	.0000	.0066	.0119	.0187	.0258	.0386	
	$K_m - K_c$	−.0002	−.0065	−.0068	−.0109	−.0190	.0363	
Ag	anx	.95						
.005 cm	K_m	.0002	.0023	.0054	.0087	.0117	.0171	
	K_c	.0000	.0063	.0112	.0176	.0245	.0368	
	$K_m - K_c$	.0002	−.0040	−.0058	−.0089	−.0128	−.0197	
Pb	anx	1.69						
.004 cm	K_m	.0019	.0115	.0169				
	K_c	.0000	.0166	.0301				
	$K_m - K_c$	.0019	−.0051	−.0132				

The atomic absorption coefficient is not generally assumed to change with any physical or chemical condition but the measurements reported here indicate that it is approximately proportional to the temperature. To show this first assume $a = a'$, giving $K_c = 2ganx$. Because K_c is positive the transmission should be greater when the absorber is hot. The observed values, K_m, of the percentage increase in transmitted x-rays due to heating the absorber together with the values, K_c, calculated on the assumption that the change is due to the usual thermal expansion only, are given in Table 1 and are presented graphically in Fig. 2.

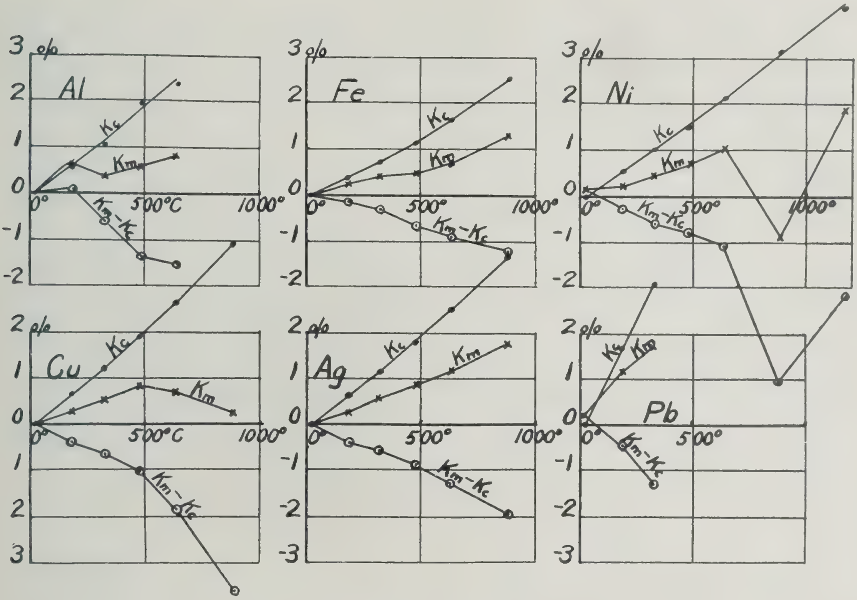

Fig. 2. Variation with temperature of the percent increase in transmission. K_m is observed and K_c calculated on the assumption that there is no variation of the atomic absorption coefficient with temperature.

To express the percentage decrease in transmission in terms of the percentage increase in absorption $(L_m - L_c)$ simply multiply by the ratio of transmitted to absorbed energy.

$$(L_m - L_c) = \frac{W_1}{W_0 - W_1}(K_m - K_c) \tag{5}$$

It will be noted that the measured change K_m was smaller than the calculated change K_c. In fact K_c was approximately twice K_m, except for a few temperatures. Therefore a' is not equal to a. These results suggest that the average atomic absorption coefficient depends on the temperature of the absorber in the following manner. Within the experimental error and for most of the temperatures and metals used

$$K_m = ganx \tag{6}$$

The true K_c given by Eq. (4) should equal K_m

$$ganx = (a - a')nx + 2ga'nx \tag{7}$$

The largest value of g was .0194 which may be neglected here when added to unity and Eq. (7) reduces approximately to

$$a' = (1+g)a\ . \tag{8}$$

This relation may be very important in the application of x-ray data to atomic structure studies. It should be confirmed by independent further measurements but unfortunately x-ray intensity measurements cannot, in the present state of the art, be measured much more accurately than was done for this work. The art of making accurate intensity measurements should be developed or new methods used for such work. Absorption coefficients are now known to three significant figures and as soon as they are measured to four figures a temperature correction will be necessary. It must be remembered that the a used above is not the usual coefficient, for a has widely different values for different wave-lengths. Only an effective value is used here. The work is being continued using narrow bands of wave-lengths and the smaller intensity of reflected x-rays makes it more difficult but not impossible to get sufficiently accurate results to show the temperature effect on absorption.

SAMPLE OF DATA AND COMPUTATION

A complete set of observations and computations is given below:

Primary, 61.0 volts, 2.8 amps.; tube current, 3.1 ± .1 m.amps.; tube filament current, 3.75 amps.; electroscope sensitivity, 173 mm per volt; temperature in the furnace, 475°C.

Run 1. Air effect, x-rays filtered through the Ag strip.

					Ave.	Diff.
Slit reading (cold):	.7812″	.7806″	.7800″	.7797″	.7804″	
						+.0072
Slit reading (hot):	.7882	.7875	.7870		.7876	

Run 2. Ag absorber (0.5 min. allowed to heat or cool off)

Slit reading (cold):	.7811	.7897	.7798	.7801	.7801	
						.0032
Slit reading (hot):	.7834	.7832	.7832		.7833	

The difference, $W_2 - W_1 = .0072'' - .0032'' = .0040''$ of the adjustable slit measures the effect of mass expanding out of the beam and any change in absorption coefficient. $(W_2-W_1)/W_1$ is the measured percentage increase in transmission due to the heating.

No absorber in balanced a slit setting of .0405″. Complete absorption by a strip of Pb balanced 1.2400″. The W_0 incident on the absorber was $1.2400-.0405=1.1995$. The Ag transmitted

$$W_1=1.2400-.7804=.4596'' \tag{9}$$

Thus

$$K_m=\frac{W_2-W_1}{W_1}=\frac{.0040}{.4596}=.0087 \tag{10}$$

$$=0.87\% \text{ change .}$$

Since

$$\frac{I_0}{I}=\frac{1.2400-.0405}{1.2400-.7804}=2.61$$

$$anx=2.30 \log \frac{I_0}{I}=0.95 \tag{11}$$

and, since for Ag $2g=16.8\times10^{-3}$,

$$K_c=2ganx=.0176 \tag{12}$$

$$K_m-K_c=-.0087+.0176=+.0089 \tag{13}$$

The Ag transmitted .89 percent less at 475°C than at 20°C or by Eq. (5) the Ag absorbed

$$\frac{.4596}{.7804-.0405}0.89\%=0.53\%$$

more at 475°C than at 20°C.

Criticism

The increase in absorption due to heating was somewhat of a surprise and it seems appropriate to criticise the method and results as follows. The balance method is good for such work but the two x-ray beams were not exactly alike, and the absorber filtered one beam.

Total radiation used had a limiting wave-length of about 0.25A. The value of anx used in computing K_c is only an effective value and the approximation

$$\exp[2ganx]=1+2ganx \tag{14}$$

may not be close enough for all wave-lengths present. If the result, K_m-K_c, were small compared to K_m more terms of the expansion should be used.

The value of K_c depends on the expansion coefficients but it is improbable that there is the 50 percent error in the latter which would be needed to make the temperature effect zero.

The absorber and the absorber holder must have warped slightly on heating. To calculate the angle of warping which would just account for the effect simply remember that approximately $K_m = 2/3K_c$ and that K_c is about 3 percent at 1000°. Thus an increase of 1 percent in the transmitted intensity when hot would make $K_m = K_c$. This requires 1.7 percent increase in anx for Al, 0.7 percent for Pb, and intermediate values for the other metals. A warping of 8° would increase x by 1 percent but that much of an angle seems improbable. No warping was observed.

No way was found to separate the effects of temperature on absorption, reflection and scattering; all are combined here.

The Braggs[8] show that the small amount of x-rays reflected from a crystal changes measurably with temperature of 370°. Collins[9] says that temperature has a marked effect on the scattered x-rays. It is suggested but not proved that the measured effect is larger than all the x-rays reflected and scattered and thus is larger than any probable change in reflection and scattering.

I wish to express my thanks to Professor F. K. Richtmyer for his pleasant interest and very generous aid. He suggested this study.

Rockefeller Hall,
Cornell University,
February, 1924.

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[8] W. H. and W. L. Bragg, X-rays and Crystal Structure, 1st ed., p. 196.

[9] E. H. Collins, Phys. Rev. **23**, 105 (1924).

NOTE ON CRYSTALLINE AND AMORPHOUS STATES IN THE ALKALI METALS

By C. C. Bidwell

Abstract

X-ray diffraction patterns obtained on a wire of metallic lithium at 20°, 80°, 110°C show a decreasing diffracting power at the higher temperatures. This is consistent with the observations of Hull and McKeehan on sodium and potassium. The obliteration of the lattice structure at the higher temperatures is correlated with changes in the thermo-electric power and resistance lines previously found by the author for all the alkali metals.

In a previous paper[1] on the resistance and thermo-electric power of the alkali metals a modification or structural change of some sort was shown to occur in the case of each of these metals, the transition being indicated by gradual changes in the resistance and thermo-electric lines. For lithium the change began to show at about +50°C, for sodium at about −40°C, for potassium about −120°C. The thermo-electric lines are straight to the transition temperature at which a gradual change in slope occurs. The resistance lines are of the form $R=R_0(1+\alpha t+\beta t^2)$ with different values for α and β after the transition temperatures are passed.

A careful study of the crystal structure of lithium at various temperatures by x-ray diffraction methods indicates that the change is not a change from one crystalline pattern to another but a gradual disintegration of the lattice with rise of temperature. For this study a squirted wire of lithium was sealed into a thin walled glass tube, one-half of which was filled with sodium chloride and flour as a comparison control. The specimen was mounted vertically in the x-ray beam and continuously rotated about its axis of cylinder. Heating was effected by a stream of warm air passing through a paper cylinder which was slipped down over the specimen. By adjusting the velocity of the air stream and its temperature, any desired temperature could be maintained within five degrees.

At 20°C a 72 hour exposure gave 5 lithium lines and 13 strong lines for the NaCl control. The lithium lines were consistent with a body-centered cube as found by Hull.[2] At 83°C a 92 hour exposure gave three lines for lithium, and again the 13 strong lines for the NaCl control. At 110°C a 76 hour exposure still showed indications of the three lithium lines but very much fainter than in the 83° exposure, while the NaCl control showed 14 lines indicating certainly no diminution in the intensity of the x-ray beam. New specimens were mounted up for each of these exposures. While the films indicate some persistence of the lattice at 110° they indicate certainly that the structure is much less definite at 110° than at 83° and less definite at 83° than at 20°.

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[1] Bidwell, Phys. Rev. **23,** 357 (1924).

[2] Hull, Phys. Rev. **10,** 661 (1917).

Hull found difficulty in getting a sample of sodium which was not amorphous at room temperature but finally succeeded in getting a pattern of seven lines corresponding to a body-centered cube. He says "the tendency to form this regular arrangement is however very slight, corresponding to a small difference between the potential energies of the crystalline and amorphous states." McKeehan[3] was able to obtain a definite crystal pattern for potassium at −150°C and states that the observed crystalline structure does not persist when the temperature is allowed to rise again to 20°C.

It is the purpose of this note to suggest that the changes indicated by the resistance and thermo-electric lines for the alkali metals may be correlated with the gradual disintegration of the crystal lattice. The thermo-electric power is particularly affected, the slopes of these lines even changing in some cases from positive to negative. The fact that these curves are not exactly reproducible on successive runs may be explained as due to the persistence in varying degree of the crystalline forms at the higher temperatures. The change in the resistance lines is not so marked out nevertheless is definite and in entire agreement as to the temperature above which the metal tends to become amorphous.

The author wishes to express his gratitude to Dr. W. R. Whitney for offering the facilities of the Research Laboratory of the General Electric Company for this work and to Dr. W. P. Davey for the use of the special x-ray equipment.

Cornell University.
December 17, 1925.

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[3] McKeehan, Proc. Nat. Acad. Sci. **8**, 8 (1922).

APRIL, 1926 PHYSICAL REVIEW VOLUME 27

A NEW KIND OF TEST OF THE CORRESPONDENCE PRINCIPLE BASED ON THE PREDICTION OF THE ABSOLUTE INTENSITIES OF SPECTRAL LINES

By Richard C. Tolman and Richard M. Badger

Abstract

The *correspondence principle* postulates a relation between the average rate at which energy is actually being discontinuously emitted by quantum transitions and the continuous rate of emission which would be calculated from the classical theory. The principle has hitherto been used to predict the *relative intensities* of spectral lines of similar origin. Since, however, the classical theory permits a claculation of absolute rates of energy emission, it should be possible to calculate from the correspondence principle the *absolute intensities* of spectral lines. In the present article, the correspondence principle is subjected for the first time to this new kind of absolute test, using Czerny's data on the intensities of the far infra-red lines Nos. 8, 9, and 10 in the pure rotational spectrum of the dipole HCl. Tests of this kind have not previously been easy to make owing to lack of information as to the experimental values of absolute intensities or lack of knowledge of the the atomic models involved. The agreement between experimental and calculated intensities is close enough greatly to increase our confidence in the correspondence principle, justify us in subjecting it to further tests, and lead us to hope that an exact quantitative formulation of the principle may be found:

I. Introduction

THE correspondence principle postulates a relation between the actual intensity of the light discontinuously emitted by the transitions of atoms from one quantum state to another, and the intensity of the light which would be continuously emitted on the basis of classical electromagnetics by the motion of the electric charges composing the atoms. The exact quantitative formulation of this relationship has not yet been discovered, although the problem has been specially considered by Kramers,[1] Hoyt,[2] Van Vleck,[3] Tolman,[4] and others. Indeed except for the case of large quantum numbers it is not even certain thay any exact relationship necessarily exists. Nevertheless, the principle has proved of extraordinary value in ruling out the occurrence of quantum transitions when on the basis of the classical theory there would be no tendency for the emission of radiation of the kind in question, and furthermore especially in the hands of Kramers (loc. cit.[1]) has permitted at least the approximate prediction of the relative intensities of a very considerable number of spectral lines. These successes of the correspondence principle make us hope that its range of application can be extended.

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[1] Kramers, Kgl. Danske. Vidensk. Selsk. Skrifter **8, III,** 287 (1919).

[2] Hoyt, Phil. Mag. **46,** 135 (1923); *Ibid.* **47,** 826 (1924).

[3] Van Vleck, Phys. Rev. **24,** 334 (1924).

[4] Tolman, Phil. Mag. **49,** 130 (1925).

In all of the tests of atomic or molecular behavior to which the correspondence principle has hitherto been subjected it has only been feasible to compare the experimental facts either with the prediction that a given spectral line will not occur at all or with a prediction as to the *relative* intensities of related spectral lines. Nevertheless, since the classical theory provides us with a method of estimating the absolute rates with which energy is absorbed or emitted by moving charges, it should be possible to predict with the help of the correspondence principle the *absolute* intensity of absorption and emission lines.

It is the purpose of the present article to subject the correspondence principle to this new kind of more exacting test by comparing experimental and theoretical values for the strength of absorption lines of hydrogen chloride in the far infra-red. Such a test of predictions as to absolute intensities has not previously been possible, either because of the very limited number of spectral lines for which we know the absolute intensity, or because we did not have sufficient knowledge as to the atomic models involved. The recent beautiful work of Czerny,[5] however, on hydrogen chloride provides us with information as to the absorption of radiation accompanying changes in the velocity of rotation of a simple electric dipole, while the measurements of Zahn[6] coupled with the calculations of Pauling[7] give us a value for the electric moment of the dipole in question. As the result of the computations thus made possible, we find an agreement between experiment and theory, which is probably as close as could be expected with our present development of experimental technique and theoretical insight. This verification of a prediction as to absolute intensities cannot fail to increase our confidence in the correspondence principle, justify us in subjecting it to further tests and applications, and lead us to hope that the principle may sometime receive a correct and precise quantitative formulation.

PART I. CALCULATION OF ABSORPTION COEFFICIENT

2. *Refinements in method of calculation.* Our first task will be to calculate from Czerny's absorption data the value of Einstein's coefficient

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[5] Czerny, Zeits. f. Physik **34,** 227 (1925).

[6] Zahn, Phys. Rev. **24,** 400 (1924).

[7] Pauling, Proc. Nat. Acad. **12,** 32 (1926).

B_{ij} which gives the probability of transition from a lower quantum state S_i to a higher state S_j by the absorption of radiation. We shall then compare the experimental value of B_{ij} with that predicted by the correspondence principle.

The method of calculating values of B_{ij} and the results obtained in a wide variety of cases are illustrated by an earlier paper of Tolman.[8] In these earlier calculations, however, the difference in the energy levels corresponding to states S_i and S_j was so large that the number of molecules in the upper state S_j was relatively very small and the reinforcement of the primary beam by induced transitions from the upper to the lower state could be neglected. Our present treatment will be refined to cover this point, since the number of molecules in the upper quantum states under consideration is large enough so that the induced emission is in the neighborhood of fifty percent of the primary absorption.

The treatment will also be modified in the direction of greater precision by not introducing into the theoretical development the assumption that the effective width of the line is small as has hitherto been customary. In the numerical application of the theory to the data in hand, however, we shall find it possible to introduce this simplification.

3. *Einstein's treatment of absorption and emission.* Calculations of the kind to be made must be based on Einstein's 1917 formulation[9] of the nature of the absorptive and emissive processes. In accordance with this formulation, if we consider a system containing N_i molecules in the lower quantum state S_i, and N_j molecules in the upper state S_j, surrounded by radiation of the frequency ν involved in the quantum transitions, we may write the following expressions governing the rates of passage of molecules between the states by interaction with radiation. For the passage of molecules from state S_i to S_j by absorption we have

$$-dN_i/dt = N_i \rho_\nu B_{ij} \tag{1}$$

where ρ_ν is the density of radiation of the frequency ν which can be absorbed, and the constant B_{ij} is Einstein's coefficient of absorption. And for the passage of molecules in the reverse direction, we may write

$$-dN_j/dt = N_j A_{ji} + N_j \rho_\nu B_{ji} \tag{2}$$

where the constant A_{ji} is Einstein's coefficient of spontaneous emission and the constant B_{ji} the coefficient of induced emission. Furthermore, as a result of Einstein's considerations we have the following relations connecting the coefficients

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[8] Tolman, Phys. Rev. **23,** 693 (1924).

[9] Einstein, Phys. Zeits. **18,** 121 (1917).

$$A_{ji}=\frac{8\pi h\nu^3}{c^3}\,\frac{p_i}{p_j}B_{ij}\,;\qquad B_{ji}=\frac{p_i}{p_j}B_{ij} \tag{3}$$

where p_i and p_j are the a priori probabilities of the two states. In applying the above equations to an absorption experiment to calculate the effect of the molecules of a medium on the transmission of a beam of light, it should be noted that each molecule which changes from the lower state S_i to the upper state S_j under the action of the light in accordance with Eq. (1) is to be regarded as abstracting a quantum of light $h\nu$ from the oncoming beam. On the other hand for the molecules which pass in the opposite direction in accordance with Eq. (2), a careful distinction must be drawn, since those dropping by spontaneous emission are to be regarded as giving off quanta $h\nu$ of random direction and phase, while those which go down by induced emission are to be thought of as giving quanta coherent with the stimulating radiation and hence reinforcing the primary beam.

4. *Modified formulation of absorption and emission.* The original formulation given above applies strictly only to a system in which the radiation that can be absorbed or emitted may be treated as having a single definite frequency ν, a condition of affairs which corresponds on the experimental side to a spectral line having no appreciable width and on the theoretical side to a system in which the molecules in a given quantum state all have exactly the same energy content. In actual systems, however, molecules in a given quantum state do not all have the same energy content, but owing to the effect of fields from neighboring molecules, to the velocity of thermal motion, and perhaps in a small degree to a fundamental lack of sharpness, the molecules in a given quantum state have a range of energies distributed around a most probable value. And hence in accordance with the fundamental equation $E=h\nu$ we obtain a range of energy changes and corresponding range in frequencies for a given quantum transition. Hence since the spectral lines in the case which we are to treat are rather broad compared with their absolute position in the frequency scale, it will be desirable to modify the original Einstein formulation.

The possibility and nature of a new formulation which will allow for the absorption or emission of a continuous range of frequencies has already been indicated by Pauli[10] and by Einstein and Ehrenfest,[11] and it is believed that the following set of relations is in agreement with their point of view. In these new relations we shall use small letters b_{ij}, a_{ji}

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[10] Pauli, Zeits. f. Physik **18,** 272 (1923).

[11] Einstein and Ehrenfest, Zeits. f. Physik **19,** 301 (1923).

and b_{ji} for the probabilities of absorption and emission, and shall regard these quantities as continuous variables which may change as we pass across a spectral line. For any given frequency ν we shall then write for the rate of passage of molecules from the lower to the higher state

$$-\frac{d(\delta N_i)}{dt}=(\delta N_i)\rho_\nu b_{ij} \tag{4}$$

and for the passage in the opposite direction

$$-\frac{d(\delta N_j)}{dt}=(\delta N_j)a_{ji}+(\delta N_j)\rho_\nu b_j \tag{5}$$

where

$$\delta N_i=\frac{\partial N_i}{\partial \nu}\delta\nu \text{ and } \delta N_j=\frac{\partial N_j}{\partial \nu}\delta\nu \tag{6}$$

are the numbers of molecules in the two quantum states which have exactly the right configuration to interact with radiation of frequency in the range ν to $\nu+\delta\nu$. Furthermore we shall also write the relations

$$a_{ji}=\frac{8\pi h\nu^3}{c^3}\,\frac{p_i}{p_j}b_{ij} \text{ and } b_{ji}=\frac{p_i}{p_j}b_{ij} \tag{7}$$

connecting the coefficients,—relations which are sufficient to guarantee agreement with the Planck radiation law.

We shall further find it convenient to retain the original Einstein coefficients B_{ij}, A_{ji} and B_{ji} by regarding them as average values for the spectral line under consideration in accordance with the equations of definition

$$B_{ij}=\frac{1}{N_i}\int b_{ij}\delta N_i\ ; \qquad A_{ji}=\frac{1}{N_j}\int a_{ji}\delta N_j\ ; \qquad B_{ji}=\frac{1}{N_j}\int b_{ji}\delta N_j \tag{8}$$

5. *Relation between the coefficient B_{ij} and the absorption coefficient α_ν.* We may now apply the foregoing considerations to the interpretation of an absorption experiment. Consider a beam of light of total intensity I in ergs cm^{-2} sec^{-1}, and let us define the intensity for a given frequency by the equation

$$I_\nu=dI/d\nu \tag{9}$$

Let the beam of light fall on a layer of absorbing medium having a cross section of one square centimeter and a thickness dx, and containing per cubic centimeter δN_i molecules in a conditions to absorb radiation in the frequency range ν to $\nu+\delta\nu$ and δN_j in a condition to emit this frequency. Since the density of radiation corresponding to the intensity I_ν is obviously given by the equation

$$\rho_\nu = I_\nu / c \tag{10}$$

where c is the velocity of light, we may evidently write, in accordance with Eqs. (4) and (5), for the rates at which molecules in the layer of unit cross section and thickness dx are passing from one condition to the other by absorption and induced emission the expressions

$$-\frac{d}{dt}(\delta N_i dx) = (\delta N_i dx)\frac{I_\nu}{c}b_{ij} \text{ and } -\frac{d}{dt}(\delta N_j dx) = (\delta N_j dx)\frac{I_\nu}{c}b_{ji} \tag{11}$$

For each molecular transition, however, one quantum of energy $h\nu$ is either absorbed or returned to the beam, so that we easily obtain from Eqs. (11) an expression for the net rate at which energy in the frequency range ν to $\nu+\delta\nu$ is absorbed from the beam because of its passage through the layer, and can write

$$-d(I_\nu \delta\nu) = (\delta N_i dx)\frac{I_\nu}{c} b_{ij}h\nu - (\delta N_j dx)\frac{I_\nu}{c} b_{ji}h\nu \tag{12}$$

By the rearrangement of (12) and introduction of the expression for b_{ji} given by (7) we obtain

$$-\frac{1}{I_\nu}\frac{dI_\nu}{dx} = \frac{h\nu b_{ij}}{c}\left(\frac{\delta N_i}{\delta\nu} - \frac{p_i}{p_j}\frac{\delta N_j}{\delta\nu}\right) \tag{13}$$

and this is evidently the ordinary absorption coefficient for light of frequency ν which may be appropriately designated by the symbol α_ν giving us

$$\frac{h\nu b_{ij}}{c}\left(\frac{\delta N_i}{\delta\nu} - \frac{p_i}{p_j}\frac{\delta N_j}{\delta\nu}\right) = \alpha_\nu \tag{14}$$

If now we assume a condition of thermal equilibrium we may write in accordance with the Maxwell-Boltzmann distribution law

$$\delta N_j = \delta N_i \frac{p_j}{p_i} e^{-h\nu/kT} \tag{15}$$

and by substitution and rearrangement obtain in accordance with the definition of B_{ij} given by (8)

$$B_{ij} = \frac{1}{N_i}\int b_{ij}\delta N_i = \frac{c}{hN_i}\int \frac{\alpha_\nu d\nu}{\nu(1-e^{-h\nu/kT})} \tag{16}$$

where the integration is to be taken across the effective width of the absorption line. This would seem to be an exact expression for B_{ij} which is the average value of the coefficient b_{ij}, and is the quantity to be compared with that obtained from the correspondence principle.

6. *Calculation of B_{ij} from Czerny's results.* In the far infra-red Czerny (loc. cit.[5]) has measured the absorption of hydrogen chloride gas corresponding to simple changes in the state of rotation of the electric dipole H^+Cl^-. In particular he gives a plot of percentage transmission as a function of wave-length in the region of lines 8, 9, and 10 which correspond to changes in the rotational quantum number m of ($7\frac{1}{2}$ to $8\frac{1}{2}$), ($8\frac{1}{2}$ to $9\frac{1}{2}$) and ($9\frac{1}{2}$ to $10\frac{1}{2}$), and although he states that exact information as to the intensities of absorption and width of line cannot be taken from the plot owing to the relatively great width of his spectrometer slit, nevertheless his results would seem to be approximately reliable. Furthermore, he states that the length of his absorption tube was 12 cm, while for the three lines in question he appears to have used hydrogen chloride gas at one atmosphere pressure and room temperature. We thus have for the three lines mentioned all the data necessary for substitution in Eq. (16).

Since, even for these lines in the far infra-red, the effective width of the lines is not great compared with their absolute position in the frequency scale, we can rewrite Eq. (16) for our purposes in the approximate form

$$B_{ij}=\frac{c}{hN_i\nu_0\left(1-e^{-h\nu_0/kT}\right)}\int a_\nu d\nu \qquad (17)$$

where ν_o is the frequency of the center of the line.

The number of molecules N_i in different states of rotation corresponding to different rotational quantum numbers

$$m=1/2,\, 3/2,\, 5/2,\, \ldots\, (i-1/2) \qquad (18)$$

can be calculated in accordance with the Maxwell-Boltzmann distribution law from the equation[12]

$$N_i=\frac{Np_ie^{-\epsilon i/kT}}{\sum_i p_ie^{-\epsilon i/kT}}=N\frac{2ie^{-(i-\frac{1}{2})^2h^2/8\pi^2JkT}}{\sum_i 2ie^{-(i-\frac{1}{2})^2h^2/8\pi^2JkT}} \qquad (19)$$

and for high temperatures may introduce the approximation

$$\sum_i 2ie^{-(i-\frac{1}{2})^2h^2/8\pi^2JkT}=\sum_i 2ie^{-(i-\frac{1}{2})^2\sigma}\approx(1/\sigma)\left[1+\tfrac{1}{2}\sqrt{\pi\sigma}\right] \qquad (20)$$

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[12] See Tolman, Phys. Rev. **22,** 470 (1923).

where N the total number of molecules per cc at one atmosphere and 20°C, can be taken as 2.52×10^{19} and the term containing J, the moment of inertia of the molecule can be taken from Czerny's own work which gives $h/8\pi^2J=10.397\ c$. The results for the three lines nos. 8, 9, and 10 are given in column two of Table I.

Values for the wave numbers ν_0/c corresponding to the centers of the lines were obtained by Czerny as given in column three, and values of the factor $(1-e^{-h\nu_0/kT})$ have been calculated and are given in column four of Table I.

Finally the values of the integral $\int a\nu d\nu$ have been obtained from Czerny's plot of percentage transmission I/I_0 as function of wave-length λ by replotting $\log I/I_0$ against $1/\lambda$ and with the help of a graphical integration substituting into the equation

$$\int a_\nu d\nu=-\frac{2.30c}{x}\int \log\frac{I}{I_0}\,d\left(\frac{1}{\lambda}\right) \tag{21}$$

where for x we use the length of the absorption tube 12 cm. The values obtained are given in column five of Table I.

We now have all the quantities necessary for substitution into Eq. (17) and obtain for B_{ij} the results given in the last column of Table I.

TABLE I

(c. g. s. units)

No. of line	N_i	ν_0/c	$(1-e^{-h\nu_0/kT})$	$\int a_\nu\, d\nu$	B_{ij}
8	0.9806×10^{18}	165.63	0.5553	3.318×10^{10}	5.61×10^{16}
9	$4.897\ \times10^{17}$	185.86	0.5970	0.425×10^{10}	6.81×10^{16}
10	$2.180\ \times10^{17}$	206.38	0.6356	1.987×10^{10}	10.59×10^{16}

PART II. THEORETICAL CALCULATIONS OF THE ABSORPTION COEFFICIENTS

7. *Application of the correspondence principle to a dipole rotator.* We must now turn our attention to the theoretical estimation of the above absorption coefficients with the help of the correspondence principle, which postulates a relation between the rates at which energy is actually emitted by molecules in accordance with the quantum theory and the rates which would be calculated on the basis of the classical theory.

Consider a system containing a number of dipole rotators all in the same quantized state of rotation S_j corresponding to the rotational quantum number m_j. It we treat the system as degenerate, i.e. not spatially quantized, the axes of rotation of these dipoles will be oriented in random directions, and the emission of radiation will result from a jump to a lower state of rotation S_i corresponding to the rotational quantum number $m_i=m_j-1$, the axis of rotation for any particular dipole retaining its direction in space.

On the basis of the *quantum theory* the average rate of emission of energy per rotator will evidently be

$$\left(\frac{dR}{dt}\right)_Q = A_{ji}h\nu \tag{22}$$

where A_{ji} is Einstein's coefficient of spontaneous emission.

On the other hand, on the basis of the *classical theory* the rate of spontaneous emission of energy by a dipole rotator would be

$$\left(\frac{dR}{dt}\right)_{Cl} = 2\times\frac{16\pi^4}{3c^3}C^2\omega^4 \tag{23}$$

where C is the electric moment of the dipole and ω the frequency of revolution.

The *correspondence principle* postulates now the existence of a relation between such pairs of expressions for the rates of energy emission, as given by the two theories. As already stated the exact formulation of this relation if it exists has not yet been discovered. It seems reasonable, however, to presume that the correct quantum theory rate of emission as given by Eq. (22) might be determined by some method of averaging the classical rates which in accordance with Eq. (23) would be calculated for the initial and final states of the rotator or perhaps for the mechanically possible intermediate states. This presumption can be symbolically expressed by the equation

$$\frac{dR}{dt} = A_{ji}h\nu = 2\times\frac{16\pi^4}{3c^3}\left[C^2\omega^4\right]_{av} = 2\times\frac{16\pi^4}{3c^3}Q^2\nu^4 \tag{24}$$

where we have introduced for convenience a new quantity Q which may be regarded as the electric moment of an idealized classical rotator having the frequency ν and desired rate of energy emission $A_{ji}h\nu$.

8. *Methods of averaging.* The method of averaging, which has received the most study and in the hands of Kramers (loc. cit.[1]) has led to excellent estimates of the relative intensities of lines, would either make the hypothetical electric moment Q merely the mean of the actual electric moments in the initial and final quantum states in accordance with the equation

$$Q = \frac{C_i + C_j}{2} \tag{K}$$

or would make the square of Q the mean of the squares of C_i and C_j in accordance with the equation

$$Q^2 = \frac{C_i^2 + C_j^2}{2} \tag{K}$$

Six methods of averaging over the mechanically possible intermediate states, one of which was proposed by Kramers, have also been studied by Hoyt (loc. cit.[2]) and by Tolman (loc. cit.[4]) and are represented by the following equations

$$Q^2=\int_0^1 C^2 d\lambda \tag{A}$$

$$Q=\int_0^1 C\, d\lambda \tag{B}$$

$$\log Q=\int_0^1 \log C\, d\lambda \tag{C}$$

$$Q^2\nu^4=\int_0^1 C^2\omega^4\, d\lambda \tag{D}$$

$$Q\nu^2=\int_0^1 C\omega^2\, d\lambda \tag{E}$$

$$\log (Q\nu^2)=\int_0^1 \log (C\omega^2) d\lambda \tag{F}$$

where λ is an auxiliary variable which is related to the phase integral ($I=\int pdq$) taken for intermediate states by the equation

$$I=I_i+\lambda(I_j-I_i) \tag{25}$$

Since for a *rigid* dipole the electric moment is a constant, four of the methods of averaging evidently lead to a simple equality of the hypothetical moment Q and the actual moment C, as shown in Table II.

TABLE II

Method of Average	Value of Q^2 for transition $(m+1)$ to m
K, A, B, C	$Q^2=C^2$
D	$\frac{16}{5}\,\frac{(m+1)^5-m^5}{(2m+1)^4}\,C^2$
E	$\frac{16}{9}\,\frac{\{(m+1)^3-m^3\}^2}{(2m+1)^4}\,C^2$
F	$\frac{16}{\epsilon^4}\,\frac{(m+1)^{4(m+1)}}{m^{4m}(2m+1)^4}$

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[13] See Tolman, *loc. cit.*, footnote 4. The treatment given in this article was worded so as to apply to a rigid dipole rotator with whole quantum numbers. The results quoted, however, are the same for the case of whole and half quantum numbers.

The results for the other three methods of averaging in terms of the rotational quantum numbers m and $m+1$ of the two states have previously been published[13] and are also given in Table II.

Substituting the values for m (7.5, 8.5 and 9.5), corresponding to the three lines under investigation, into the expression given by methods D, E, and F of averaging, we find that these methods also give within one percent the same value

$$Q^2=C^2 \tag{26}$$

and hence we shall use this in our following calculations. It is indeed fortunate that we have data to test so simple a case as that of a rigid dipole rotator, since it seems probable that for any reasonable method of averaging, expression (26) would give at least the right order of magnitude for Q^2.

9. *Relation between B_{ij} and Q^2.* To calculate the theoretical value of Einstein's coefficient of absorption B_{ij} from the value of Q^2 we have merely to combine Eqs. (3) and (24) in the text and obtain

$$B_{ij}=2\times\frac{2\pi^3}{3h^2}\,\frac{p_j}{p_i}Q^2 \tag{27}$$

10. *Numerical value of Q and theoretical values of B_{ij}.* The measurements by Zahn[6] of the dielectric constant of hydrogen chloride gas make it possible to calculate the electric moment of the dipole and this has been done by Pauling[7] in accordance with the theory of half quantum numbers. He obtains the value 0.3316×10^{-18} in C.G.S. electrostatic units.

Taking this as the value of Q and substituting in Eq. (27) we obtain for B_{ij} the values 10.9, 10.8, and 10.7×10^{16} for the successive lines Nos. 8, 9, and 10.

11. *Application of correspondence principle treating the system as non-degenerate.* In the foregoing calculations, as noted above, we have treated the dipole rotators as degenerate systems, with their axes of rotation distributed in random directions. It has been suggested by Kemble,[14] however, in considering rotation-oscillation spectra, that the correspondence principle ought to be applied to such systems by treating them as though they had been made non-degenerate by spatial quantization in a weak external (magnetic) field.

Under these circumstances, the axes of rotation can only assume certain spatially quantized directions and we must use two quantum numbers to describe the state of the rotator, a rotational quantum number m

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[14] Kemble, Phys. Rev. **25,** 1 (1925).

which is proportional to the total angular momentum of the rotator, and an equatorial quantum number r which is proportional to the component of the angular momentum parallel to the applied field, the angle between the axis of rotation and the external field being given by the equation $\cos\theta = r/m$. The possible absorption processes may then be correlated with a change in the rotational quantum number from m to $m+1$ and changes in the equatorial quantum number from r to $r \pm 1, 0$. Furthermore each of these processes may be correlated with terms in the Fourier analysis for the motion of the rotator, and the frequency of occurrence of the different transitions estimated from the magnitude of the coefficients of the corresponding terms in the Fourier analysis.

We have also made an estimation of the intensities of the three lines in question on this basis. The calculation is complicated by the fact that the Fourier coefficients corresponding to a given quantum transition now have in general different magnitudes in the initial and final state of the molecule, since they depend on the angle between the external field and the axis of rotation and in general this changes when the transition occurs. In order to overcome this difficulty, following the procedure of Kemble, we have determined the Fourier analysis for an intermediate motion, in which the angle between the external field and axis of rotation is given by the equation $\cos\theta = \bar{r}/\bar{m}$, where $\bar{r}$ and $\bar{m}$ are the respective means of the values of the quantum numbers r and m in the initial and final state. We have then used the Fourier coefficients of the proper terms in the analysis of this intermediate motion as the amplitudes of the idealized classical motions of frequency ν which on the basis of the correspondence principle may be assumed to give the same rate of energy emission as the average rate given by the quantum transition in question.

We do not reproduce the calculations here, since they are somewhat lengthy, and for the particular absorption lines under consideration lead nearly to the same results as our previous simpler calculations which treated the rotators as degenerate systems. The approximate agreement of these new results obtained by treating the rotators as non-degenerate is due to the fact that the theory of spatial quantization prescribes no less than sixteen values of the angle between field direction and precessing axis even for the molecules of lowest energy content involved in the production of lines Nos. 8, 9, and 10, and the changes in direction of the axis accompanying the permitted transitions are small. Hence the spatially quantized system of rotators behaves nearly the same as a degenerate system in which the axes of rotation are uniformly distributed in direction and there is no change in direction when a quantum transition takes place. For the first lines in the rotational spectrum the two methods of treatment lead to quite different results. For this reason an experimental determination of the intensities of these lower lines would be interesting.

12. *Newer methods of treatment.* In addition to the methods of applying the correspondence principle discussed above, there has recently been considerable investigation of the calculation of intensities by methods specially adapted to agree with the Burger Dorgelo "sum rule" for the intensities of the components of a multiplet line. These methods may be called with Fowler "refined applications" of the correspondence principle. In particular Professor J. H. Van Vleck has been good enough to call our attention by letter to an article by Reiche and Thomas[15] in which an expression has been obtained for the absolute intensity of the pure rotational lines for a dipole rotator. It is interesting to note that their expression (see page 521 l.c.) becomes identical with our equation (27) obtained from methods of averaging K, A, B, C, provided we modify their equation in such a way as to allow for the fact that the electric separation in the hydrogen chloride molecule is different from the internuclear distance, and further substitute the same a-priori weights which we have employed. Hence we may regard our calculations as also agreeing with the work of Reiche and Thomas.

It should also be noted that the new quantum mechanics of Born and Heisenberg is specially adapted for the calculation of intensities of lines, but we have not yet carried through a calculation along these lines. To do this, it would first be necessary to consider whether, by going over to the new basis, modifications might not have to be introduced into Pauling's calculation of electric moment.

PART III. COMPARISON OF EXPERIMENTAL AND THEORETICAL VALUES OF B_{ij}

13. *Conclusion.* We may now compare the experimental values of B_{ij} calculated from Czerny's absorption measurements with the theoretical values calculated from the correspondence principle, as given below in the last two columns of Table III.

TABLE III

No. of line	Transition	B_{ij}(exp.)	B_{ij}(theor.)
8	$m = 7.5$ to $m = 8.5$	5.6×10^{16}	11.9×10^{16}
9	$m = 8.5$ to $m = 9.5$	6.8×10^{16}	11.8×10^{16}
10	$m = 9.5$ to $m = 10.5$	10.6×10^{16}	11.6×10^{16}

The agreement is not exact, and perhaps outside the experimental error of the two sets of measurements of Czerny and Zahn which were used in the calculations. Nevertheless when we consider the difficulties of both kinds of experimental work and the complexity of the three calculations by which the electric moment was obtained from the measurement of dielectric constant, and Einstein's coefficient was calculated first from the absorption measurements and then from the correspondence principle, the results are certainly of a nature to increase our respect for the correspondence principle, which has now been subjected for the first time to this kind of *absolute* test, involving the absolute rather than the relative intensities of spectral lines.

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[15] Reiche and Thomas, Zeits. f. Physik, **34**, 510 (1925).

The most striking characteristic of the lack of agreement is the gradual rise in the experimental values of B_{ij} as we go to higher quantum numbers approaching perhaps the nearly constant value predicted from the correspondence principle. This may indicate the necessity of a progressive modification of the correspondence principle as we go to lower quantum numbers, a possibility which finds some support from other directions. Speculations, however, as to the precisely correct manner of applying the correspondence principle can best be postponed until more certain experimental data are at hand. An attempt to obtain further data for this purpose is already under way in this laboratory.

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THE ARC SPECTRA OF IODINE, BROMINE, AND CHLORINE IN THE SCHUMANN REGION

By Louis A. Turner

ABSTRACT

The arc spectra of Cl, Br, and I have been investigated in the region between 2050 and 1230 A. U. Wave-length tables are given. 1396.5 and 1633.6 A. U. are the wave-lengths of the lines of longest wave-length of Cl and Br, respectively, and correspond to the previously known 2062.1 line of I. Doublet differences of 881, 3685, 7600 wave number units are found between lines of Cl, Br, and I spectra respectively and are thought to be the separations of the two levels of normal doublet *p* states of the atoms. The probable resonance lines are of wave-lengths 1379.6, 1540.8 and 1782.9 A. U. corresponding to radiating potentials of 8.95, 8.01, and 6.92 volts. No band spectrum of HCl appeared in the region investigated although the excitation was probably favorable for its production.

SEVERAL investigators[1,2,3] have observed four very intense spectrum lines, emitted by mildly excited iodine vapor, in the region of the shortest wave-lengths which can be photographed with a quartz spectrograph. Their great intensity and the conditions for their excitation[3] suggested that these lines were probably arc lines arising from transitions between low energy levels of the atom, and that more strong lines which might show simple spectrum relationships would be found in the Schumann region. The study of this region of the spectrum was made possible by Professor T. Lyman who very kindly permitted me to use his vacuum spectrograph.

APPARATUS AND METHODS

The vacuum spectrograph has been fully described elsewhere.[4] The grating was one of 1 meter focus with 15,000 lines to the inch, ruled by Professor R. W. Wood at Johns Hopkins University. Experience has shown it to give spectra nearly free from ghosts of the Lyman type. A fluorite plate was placed over the slit to prevent the halogen vapors from entering the body of the spectrograph, consequently the shortest wave-length which could be measured was about 1230 A.U. The grating was so set that the longest wave-length observed was 2050 A. U. The

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[1] E. B. Ludlam and W. West, Proc. Roy. Soc. Edinburgh **44 II,** 185 (1923–24).

[2] C. Füchtbauer and E. Holm, Phys. Zeits. **26,** 345 (1925).

[3] R. S. Mulliken and L. A. Turner, Phys. Rev. **25,** 886 (1925).

[4] T. Lyman, Astrophys. J. **50,** 1 (1924).

spectra were photographed in the first order, the dispersion being 16.84 A. U. per millimeter.

The discharge tube had tungsten wire electrodes and an internal capillary tube placed close to the slit (Fig. 1). For nearly all of the exposures a continuous current of 10–15 milliamperes supplied by an arrangement of a transformer, kenetron rectifiers, and a large condenser, was used. This type of apparatus favors the production of spectra requiring only moderate excitation, as has been found in work with other elements. That such is the case was shown in these experiments with iodine by the great intensity of the band spectrum in the visible region as observed through the outer end of the discharge tube. Furthermore, three of the lines previously known to be excited strongly by active nitrogen and in a carbon arc,[3] were among the strongest of the lines obtained with the continuous current. Consequently, the spectra produced with this excitation have been designated as arc spectra. Different spectra were observed when an ordinary condensed spark discharge was used.

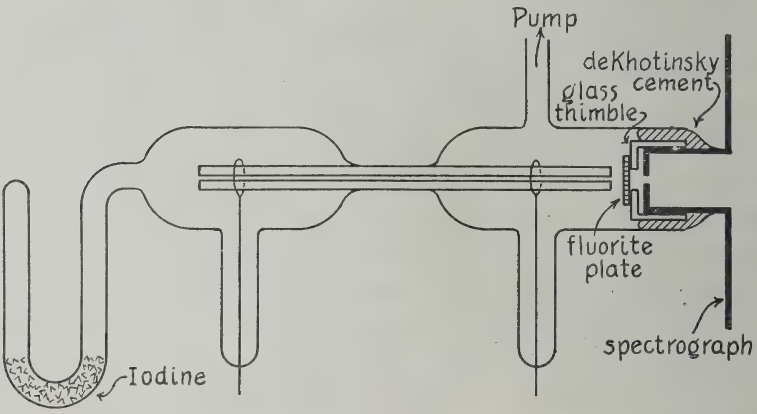

Fig. 1. The discharge tube.

Great difficulty was experienced with the frequent appearance, on the fluorite window, of thin films which were opaque to the light of short wave-lengths. The presence of a small amount of air or water vapor would cause the rapid appearance of such a film. The deKhotinsky cement, used to fasten the discharge tube to the spectrograph, was acted on by the halogen vapors and may have been a further source of impurities which caused these films. The region of the tube surrounding the positive electrode quickly became coated with a dark deposit but no such deposit formed around the negative electrode. Accordingly the electrode nearest the window was always made negative. It was found that the window would remain clean if the discharge tube were connected to the pump continuously through a liquid air trap. It was expected that these various impurities would give spectrum lines of their own but that such lines would be found in both the iodine and bromine spectra.

The standards of measurement used were lines of the many-line spectrum of hydrogen measured by Lyman[5] and the iodine line at 1876.40 measured by R. S. Mulliken and the author.[3] The wave-lengths of these hydrogen lines were originally estimated to be correct to within 0.3 A.U. but subsequent work has shown them to be considerably more accurate. The wave-lengths of the lines of the halogens should be accurate to 0.2 A.U.

IODINE

For obtaining the iodine spectra an appendix containing ordinary resublimed iodine was attached to one end of the discharge tube. It was kept in melting ice. The other end of the discharge tube was continuously connected to the pump through a liquid air trap. There was, therefore, a pressure gradient in the iodine vapor through the system, the maximum pressure being 0.03 mm. The flow of the iodine vapor tended to sweep out impurities. When the discharge tube was closed off from the liquid air trap the CO bands came out strongly and some of the strongest iodine lines were tremendously reduced in intensity. Others of the strong lines were apparently unaffected. The lines which show this reduction markedly are indicated in the list of lines of Table 1. This effect did not occur when the discharge was passed through a mixture of hydrogen and iodine. A few spectra were obtained with a different discharge tube having large external tinfoil electrodes, excited by the transformer alone. The spectra thus obtained were practically the same as those given by the continuous current discharge but of lower intensity. One exposure was obtained by passing a condensed spark discharge from a small transformer through the tube with the internal electrodes. In this exposure the fluorite window was quickly coated over but several strong new lines appeared on the plate. None of the most intense arc lines was present, however. The three lines marked with an asterisk in Table 1 were present in this spark exposure with moderate intensity, much less than that of several other new lines, however. No attempt was made to measure the wave-lengths of the spark lines because of the lack of a comparison spectrum for fixing the position of these lines with respect to the standards. Table 1 gives

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[5] T. Lyman, Memoirs Am. Acad. Arts and Sci., **XIII, III** (1906). Also "The Spectroscopy of the Extreme Ultraviolet."

TABLE I

Iodine

Intensity	Wave-length	Wave-number	Intensity	Wave-length	Wave-numbe
10	†2062.1	48494	5	1390.9	71897
7	1876.4	53293	3	1383.4	72286
9	1844.5	54216	0	1382.3	72342
10	+1830.4	54632	3	1368.3	73084
7	1799.2	55581	2	1367.7	73114
00	1789.6	55879	0	1366.6	73173
9	+1782.9	56089	5	1361.2	73465
8	1702.3	58744	3	1358.1	73631
1	1675.4	59690	6	1355.5	73775
7	+1642.5	60885	00	1354.3	73841
7	1641.1	60934	00	1352.4	73942
1	1639.2	61005	1	1350.3	74055
6	+1617.9	61809	1	1349.0	74128
6	1593.8	62742	1	1343.7	74420
1	1582.8	63179	2	1340.9	74579
1	1545.9	64685	0	1339.9	74631
4	+1526.6	65505	6	1336.7	74810
7	1518.3	65863	2	1330.4	75167
9	1514.8	66014	3	(1317.7)	75893
3	1507.3	66342	1	1314.1	76099
5	1493.2	66971	0	1313.6	76124
1	1486.1	67289	1	1303.2	76735
00	1466.7	68179	2	*1300.6	76888
5	1466.0	68210	0	1296.6	77127
6	1459.2	68528	1	1291.4	77437
6	+1458.2	68579	1	1289.6	77541
4	1457.6	68606	2	*(1286.3)	77742
4	1453.4	68806	0	1277.4	78281
5	1446.5	69131	2	*1275.7	78386
0	1429.7	69947	2	(1259.4)	79400
8	1425.7	70143	3	1234.2	81024
4	1421.6	70345			
3	1400.2	71421			
00	1395.0	71685			
2	1393.3	71769			

† This line lies outside of the region here investigated but previous work shows it to belong to this group. Its intensity is therefore uncertain, but is certainly much greater than that of 1876.4

+ Greatly reduced in intensity when the CO bands appear.

( ) Coincide with lines obtained with bromine.

* Possibly spark lines.

the estimated photographic intensities, the wave-lengths, and the wave-numbers of the arc lines.

BROMINE

Pure Kahlbaum bromine was placed in a small bulb which was connected to the discharge tube through a very fine capillary tube. As before, the discharge tube was connected continuously to the pump through a liquid air trap. The proper size of capillary to reduce the bromine pressure to the right amount was found by trial. The pressure was further adjusted by altering the temperature of the bulb and capillary so that a current of 10 milliamperes would flow through the tube when the conditions of excitation were the same as with the iodine. No attempt was made to measure the bromine pressure in the tube. If it were changed much either way the discharge would not pass. One spectrum was obtained with the condensed spark discharge. As with iodine, the strong lines of the spark spectrum were new ones. The strong arc lines appeared faintly. Table 2 gives the intensities, wave-lengths, and wave-numbers for the arc lines.

TABLE II

Bromine

Intensity	Wave-length	Wave-number	Intensity	Wave-length	Wave-number
10	1633.6	61214	0	1400.8	71387
8	1582.4	63194	0	1397.5	71558
6	1576.5	63432	0	1394.5	71710
9	1575.0	63492	0	1391.3	71875
6	1540.8	64902	8	1384.6	72224
7	1531.9	65277	1	[1379.6]	72485
8	1488.6	67176	0	[1363.5]	73341
0	1484.0	67383	0	[1351.7]	73981
2	1477.1	67699	1	[1347.3]	74224
0	1468.2	68111	0	[1335.6]	74869
0	1466.4	68192	6	(1317.8)	75884
4	1463.4	68336	5	1316.9	75937
0	1459.9	68498	5	1310.0	76335
1	1457.0	68633	1	(1286.4)	77735
3	1449.9	68968	2	1279.7	78145
0	1442.3	69335	1	1266.3	78969
0	1435.8	69646	1	1261.8	79253
2	1423.0	70276	2	(1259.4)	79406
2	1416.5	70597			
1	1411.5	70847	1	1255.9	79621
1	1410.1	70915	4	1251.8	79886
0	1407.1	71070	0	1249.7	80017
0	1405.1	71167	2	1244.0	80384
0	1403.6	71243	5	1232.5	81137

( ) Coincide with lines obtained with iodine.
[ ] Coincide with lines obtained with chlorine.

CHLORINE

It was not convenient to prepare and handle pure chlorine gas so the chlorine spectrum was obtained by the use of compounds. One set of exposures was made to a continuous current discharge in hydrogen chloride gas. The hydrogen chloride was generated by warming a mixture of potassium acid sulphate and sodium chloride, and was dried by passing it over phosphorous pentoxide. Its pressure was governed by the amount of warming and the adjustment of a stopcock. As with bromine the pressure was adjusted until it gave a discharge which behaved satisfactorily. The spectrum consisted of the many-line spectrum of hydrogen and seven strong lines. These same seven strong lines were the only prominent feature of a spectrum obtained from carbon tetrachloride which was used with a bulb and capillary in the same way as bromine. Consequently, the seven lines are ascribed to chlorine, the common element. Table 3 gives the data for these lines. Two of them agree within the limits of error with the two lines of wave-lengths 1351.6 and 1347.2 A.U. found by Millikan,[6] along with many other lines, in the hot-spark spectrum of chlorine.

TABLE III

Chlorine

Intensity	Wave-length	Wave-number
3	1396.5	71607
4	1389.9	71946
5	(1379.6)	72484
5	(1363.5)	73342
3	(1351.7)	73979
5	(1347.2)	74225
2	(1335.8)	74863

( ) Coincide with lines obtained with bromine.

It is of interest to note that there was no trace of a band spectrum which could be ascribed to the HCl molecule, although the excitation was probably most favorable for its production, if there is such a spectrum. Barker and Duffendack[7] found no band spectrum of HCl between 6000 and 2000 A.U. The present work places the lower limits at 1230 A.U. Apparently there is no electron transition in the HCl molecule of energy value between 2 and 10 volts. The non-existence of this band spectrum is in accord with Mulliken's[8] ideas concerning the instability of energized polar molecules.

IMPURITIES

It is not certain that all of the lines listed in the above tables actually belong to the elements to which they are ascribed because some of them may have been emitted by the impurities unavoidably present. Since the substances used were quite pure they must have resulted principally from contamination from the electrodes and the deKhotinsky cement. Any lines emitted by such impurities should appear in the spectra of all three elements. Three of the less intense lines which are common to the iodine and bromine spectra may be of this sort. The exposures made with the chlorine compounds were shorter so that these lines might not have shown on the plate even if present. The longest exposures were made with iodine so it may be that some of the weakest lines in its spectrum are those of such impurities but that they are not found in the bromine spectra because the exposures were too short to bring them out. Carbon and oxygen are probable impurities but their principal arc lines are not present. Five of the strong chlorine lines appear faintly in the bromine spectrum with the same relative intensities, indicating that the bromine used contained a small amount of chlorine. It is impossible, of course, to eliminate lines produced by an impurity present with only one of the halogens.

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[6] R. A. Millikan, Phys. Rev. **23,** 1 (1924).

[7] E. F. Barker and O. S. Duffendack, Phys. Rev. **26,** 339 (1925).

[8] R. S. Mulliken, Phys. Rev. **26,** 29 (1925).

Discussion

The most striking characteristic of these spectra is the progression of the long wave-length limits of the spectra towards longer wave-lengths with increasing atomic number. The minimum possible values of the radiating potentials, corresponding to the lines of longest wave-length, are thus fixed at 8.9, 7.6, and 6.0 volts for chlorine, bromine, and iodine, respectively. There are no indications of the convergence of iodine lines to a limit near 1400 A.U., the value corresponding to Smyth and Compton's[9] determination of the ionization potential of atomic iodine.

It was established by Paschen that the lines of the neon spectrum converge to two limits differing by 782 wave number units and Grotrian[10] showed the identity of these limits with the L x-ray absorption limits of the relativity doublet. Apparently the Ne^+ ion can exist in two different states differing in energy by an amount corresponding to the 782 wave number units. One would expect the neutral fluorine atom, having the same electron structure, to exist in two such states. The same should apply to the other halogen atoms which all presumably have similar outer structures. This is in accord with Pauli's[11] conclusion that the normal state of an atom lacking one electron from a completed group has the same multiplicity and inner quantum numbers as an atom having one extra electron of the same azimuthal quantum number. The normal state of these atoms should thus be a doublet p state. If it is double (or, to put it another way, if there is an excited state close to the normal one) the energy difference between the two states should show itself as a frequently recurring doublet difference between lines of these spectra.

[9] H. D. Smyth and K. T. Compton, Phys. Rev. **16,** 501 (1920).

[10] W. Grotrian, Zeits. für Physik, **8,** 116 (1921).

[11] W. Pauli, Zeits. für Physik **31,** 765 (1925).

Each pair of lines corresponding to transitions from a given initial level to these two final levels should have this doublet difference.

The following differences, which are equal within the limits of the experimental error, are found between the wave numbers of the iodine lines. The estimated intensities are given in parentheses.

(9) 56089 – (10) 48494 = 7595
(7) 60885 – (7) 53293 = 7592
(6) 61809 – (9) 54216 = 7593
(1) 63179 – (8) 55881 = 7596
(3) 66342 – (8) 58744 = 7598
(6) 68528 – (7) 60934 = 7594
(4) 70345 – (6) 62742 = 7603
(3) 72286 – (1) 64685 = 7601
(5) 73465 – (7) 65863 = 7602
(00) 73942 – (3) 66342 = 7600
(2) 74579 – (5) 66971 = 7608
(0) 76124 – (6) 68528 = 7596

The fact that two of the lines appear twice indicates that some of these differences are the same purely by chance. On the other hand, the inclusion of so many of the strong lines is a point in favor of the reality and significance of this difference. Other recurring differences have been found but no other which groups as many lines or includes nearly as many of the strong lines of the spectrum.

Two such differences are found with the bromine lines. The wave numbers are as follows.

(9) 63492 – (10) 61214 = 2278
(10) 67176 – (6) 64902 = 2274
(0) 69646 – (0) 67383 = 2273
(1) 70915 – (1) 68633 = 2282
(0) 71243 – (2) 68968 = 2275
(1) 80017 – (2) 77735 = 2282

(6) 64902 – (10) 61214 = 3688
(8) 67176 – (9) 63492 = 3684
(3) 68968 – (7) 65277 = 3691
(0) 71387 – (2) 67699 = 3688
(0) 71875 – (0) 68192 = 3682
(1) 79621 – (5) 75937 = 3684
(1) 80017 – (5) 76335 = 3682

The second difference of 3685 units is more probably the significant one because it includes more of the strong lines.

Six of the chlorine lines can be grouped into three pairs as follows.

(5) 72484 − (3) 71607 = 877
(5) 74225 − (5) 73342 = 883
(2) 74863 − (3) 73979 = 884

More accurate wave-length determinations must be had before a final decision can be made as to the reality of these recurring differences. Nevertheless, it seems highly improbable that the results with iodine and chlorine, at least, can be a matter of chance. If these three differences of 881, 3685, and 7600 units are the differences between the energies of the two lowest states of the respective atoms the resonance lines are those of wave-lengths 1379.6, 1540.8 and 1782.9 A.U. and the radiating potentials 8.95, 8.01, and 6.92 volts for chlorine, bromine and iodine, respectively. The reasons for believing the resonance line of iodine to be other than the 2062.1 line have been discussed elsewhere.[12] The 2062.1 and 1782.9 lines are the pair of longest wave-length which have the doublet difference.

In a recent paper Dymond[13] has shown that experiments on the fluorescence of molecular iodine indicate that the iodine atom has an excited state 1.1 volts above the normal state. The frequency difference of 7600 wave number units found here corresponds to an energy of 0.94 volts. It agrees very well with a value of 0.9 volt calculated by Franck by extrapolation from the neon frequency difference, to which Dymond briefly refers. Dymond's value is in error by the same amount as the value for the heat of dissociation of molecular iodine of 1.4 volts, which he uses. The discrepancy may be due to an error in this quantity, which is a difficult one to determine accurately, although it seems rather large to be accounted for in this way.

Hopfield[14] has shown that the normal level of the oxygen atom and of the sulfur atom is triple and Pauli[11] has given theoretical reasons for expecting it to be quintuple. We should expect a halogen ion of similar electron structure to have that same multiplicity. If so, the arc spectra of these elements must have lines converging to either three or five different limits (just as the neon spectrum converges to two limits). The great complexity of these spectra is thus quite easily understandable.

It might also be noted that if the normal state of the halogen atom is double one would expect to find two electron affinity spectra for each element, with the doublet difference between them. The one of shorter wave-length would appear only under conditions where a considerable

[12] Louis A. Turner and K. T. Compton, Phys. Rev. **25,** 791 (1925).

[13] E. G. Dymond, Zeits. für Physik **34,** 553 (1925).

[14] J. J. Hopfield, Phys. Rev. **21,** 710 (1923); Nature **112,** 437 (1923).

fraction of the atoms was in the higher of the two low states. So far as I am aware, such a doubling has never been noted in connection with the spectra ascribed to the electron affinity process.

I am greatly indebted to Professor Lyman for allowing me to use his spectrograph, and to his laboratory assistant, Mr. H. W. Leighton, for great help in performing the experiments. I also wish to thank Professor Lyman and Professor F. A. Saunders for their interest in this work and their helpful suggestions.

This work was done at the end of my year as National Research Fellow at Harvard University. I wish to take this opportunity to express my indebtedness to the National Research Council for making this year possible, and to thank all the members of the Physics Department of Harvard University for their courtesy and helpfulness which made it most profitable and pleasant.

Palmer Physical Laboratory,
Princeton University.
December 12, 1925.

Note added with proof April 6, 1926:

These $p_1 - p_2$ differences of 881, 3685, and 7600 wave number units, expressed in volts, are 0.11, 0.45, and 0.94 volts. They are in good agreement with the values 0.1, 0.5, and 0.9 predicted by Franck,[15] by extrapolation from the Ne^+ doublet difference. They also agree fairly well with the values calculated by Franck,[15] and by Wolf,[16] from the wave-lengths of the edges of the continuous absorption regions and heats of dissociation of the halogen molecules. Granting the correctness of the theoretical explanation of these continuous bands given by Dymond, Franck, and Wolf, accurate determinations of their wave-lengths combined with these doublet differences will give the most accurate values for the heats of dissociation of these molecules. The heat of dissociation of the iodine molecule so determined from Dymond's measurement of the edge of the band is $2.47 - 0.94 = 1.53$ volts, or 35.3 kg cal. per gram mol.

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[15] J. Franck. Address given before the Faraday Society. To appear in the Transactions of that society.

[16] K. L. Wolf, Zeits. f. Physik **35**, 490 (1926).

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THEORY OF CURRENT TRANSFERENCE AT THE CATHODE OF AN ARC

By J. Slepian

Abstract

The relatively low temperature of the cathode in the case of such metals as copper and mercury, suggests that thermionic emission from the cathode is not essential and that some other factor may be more important in determining the current carried to the cathode in such cases. It appears that if the gas next to the cathode is sufficiently hot, thermal ionization in accordance with Saha's equation may account for much of the current to the cathode. Calculation shows that an upper limit for the required temperature is somewhat in excess of 4000°K for Ca, and 6000°K for Cu.

Introduction

Although it is generally accepted that a cathode hot enough for thermionic emission is a necessary condition for the existence of an arc, a number of observations have been made which cast serious doubt upon the universal necessity of this condition. By an arc, is here meant a self-maintaining discharge with a drop at the cathode very considerably less than the normal cathode drop for the particular cathode material and adjoining gas in question. Thus H. Stolt[1] found that by sufficiently rapid motion of an arc over its cathode, the cathode would give no evidence of having been subjected to a very high temperature, and the author[2] has shown that transition from a glow discharge to an arc may take place while the cathode is still cold.

The case for the necessity of a thermionically active cathode has been very ably presented in a notable paper by K. T. Compton[3] who concludes that the greater part of the current carried at the cathode is by electrons emitted thermionically. However, the most convincing examples which Compton gives are the carbon and tungsten arc, in which because of the refractory properties of the materials, the cathodes may reach such high temperatures that their thermionic emission is sufficient to account for most of the current. For more volatile materials, such as mercury or copper, the thermionic theory meets a very serious difficulty in that it calls for a cathode temperature far in excess of the boiling point of the cathode material, whereas Hagenbach and Langbein,[4] in the case of copper, iron, and nickel find by optical methods that the temperatures of the cathodes are actually very near their boiling points.

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[1] Stolt, Zeits. f. Physik **26,** 95 (1924).

[2] Slepian, Jour. of Franklin Inst. (Jan. 1926).

[3] K. T. Compton, Phys. Rev. **21,** 266 (1923).

[4] Hagenbach and Langbein, Arch. Gen. **461,** 329 (1918).

Thermal Ionization in an Arc, and Theory of Cathode

In the paper by K. T. Compton referred to above, the theory is very convincingly presented that in the positive column of an arc, the ionization is maintained principally by the high temperature existing there. Using Saha's equation[5] Compton calculates the degree of ionization to be expected at 4000°K, and finds it sufficient to account for the observed conductivity in the positive column of the arc.

It appears now that this theory of thermal ionization in the arc may be used also to explain the passage of current to the cathode, so that it is no longer necessary for the cathode to have a large electron emission or to be heated to a higher temperature than its boiling point. In fact, the thermal ionization in the gas, with reasonable assumptions as to temperature, is such that the arc current may be carried to the cathode by thermally generated positive ions.

Quantitative Test of Theory of Cathode

To be sound, this theory of the cathode must meet certain quantitative tests. First, the observed cathode drop must be sufficient to carry the necessary current density of positive ions to the cathode. Second, the product of cathode drop and current density must more than make up for the heat lost from the hot gas to the relatively cold cathode.

Langmuir[6] has shown that when a plane electrode in contact with an ionized gas is given a sufficiently negative potential to repel all electrons, the current density flowing to the electrode and carried entirely by positive ions will be independent of the potential and equal to the random positive ion current density in the gas. This random current density, I, is defined as the current corresponding to the number of positive ions per second which pass in one direction through a square centimeter of an imaginary plane in the body of the gas. According to Langmuir,

$$I=\tfrac{1}{4}\, n\, v\, e \tag{1}$$

where n is the number of positive ions per cm^3, v is the average translational velocity of the thermal agitation of the ions, and e is the electronic charge.

The theory of the cathode here being developed, then, clearly requires that I given by (1) shall also be the current density at the cathode.

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[5] Saha, Phil. Mag. **40,** 472 (1920).

[6] Langmuir, G. E. Rev. **27,** 449 (1924).

If n_1 is number of molecules per cm³ in a gas at temperature T, then

$$n = n_1 \cdot x/(1+x) \tag{2}$$

where x is the fraction of molecules thermally ionized and is given by Saha's equation for atmospheric pressure,

$$\log \frac{x^2}{1-x^2} = -\frac{5050\ V_i}{T} + 2.5 \log T - 6.69 \tag{3}$$

V_i being the ionizing potential of the gas in volts.

For the velocity of agitation v of the ions, we have

$$\frac{1}{2}\frac{M}{N}v^2 = \frac{1}{2}kT\ , \tag{4}$$

M being the molecular weight of the ion, N the number of molecules in a gram molecule of substance, and k Boltzman's constant. Also

$$n_1 = n_0 \cdot 273/T \tag{5}$$

where n_0 is the number of molecules per cm³ of a gas at 273°K. Substituting (2), (4) and (5) in (1), we obtain

$$I = \frac{273}{4} n_0 e \frac{x}{1+x} \sqrt{\frac{Nk}{MT}} \tag{6}$$

For calcium we have $M=40$, $V_1=6.01$, and for copper $M=63.5$ and $V_i=7.69$. Substituting these values in (3) and (6), and taking $n_0=2.70 \times 10^{19}$, $e=4.77\times 10^{-10}$, $N=6.06\times 10^{23}$, $k=1.37\times 10^{-16}$ the curves of Fig. 1 have been calculated.

Now the current density at the cathode of an arc is of the order of 100 amperes per cm² at atmospheric pressure. Examining Fig. 1, we see that for calcium and copper the temperatures of the vapors need to be from 4000° to 5000°, and 6000° to 7000° respectively for the positive ion density to be sufficient to carry the current to the cathode.

These temperatures are rather higher than those determined experimentally, but two considerations will serve to make these figures acceptable. First of all, this high temperature needs to exist only in a thin layer of gas next to the cathode and will therefore be very difficult to detect experimentally. Secondly, Saha's equation, which is the basis of this calculation, was derived on the supposition of thermodynamic equilibrium. But an ionized gas in an electric field is not in thermodynamic equilibrium, since the electrons take energy from the electric field and maintain themselves with a greater energy of agitation than that of the neutral molecules. Thus Langmuir[7] finds that in a mercury arc the electrons have a temperature of over 10,000°K in a gas of less than 400°K. For a gas in an intense electric field therefore, the temperature (of the neutral molecules) necessary for a given degree of ionization will be much less than that called for by Saha's equation.

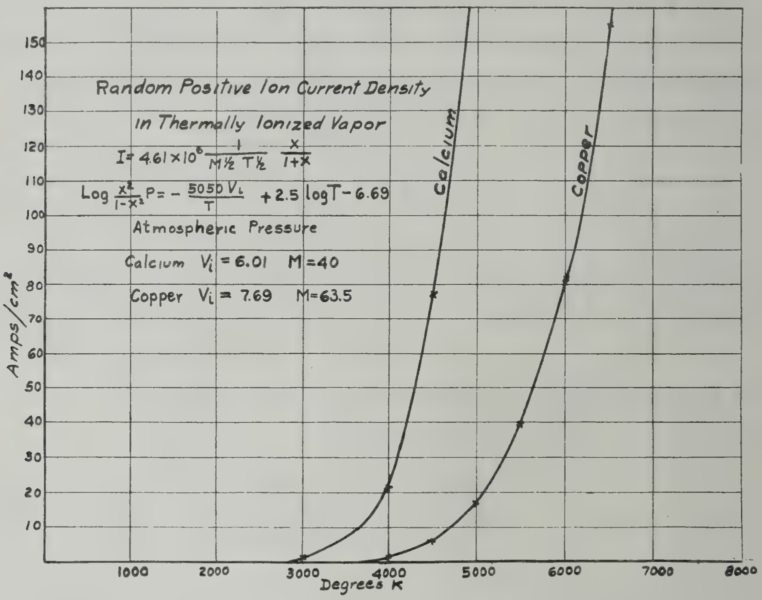

Fig. 1. Calculated variation of the temperature of the thermally ionized vapor with current density.

The electrode receiving the current of positive ions, as Langmuir has shown, is separated from the main body of ionized gas by a sheath containing only positive ions and neutral molecules, the electrons being repelled out of this sheath by the electric field. The thickness of this sheath varies with the applied potential, the applied potential being balanced by the space charge in the sheath. Langmuir gives the equation

$$I = \frac{2.336\times10^{-6}}{\sqrt{1834M}}\,\frac{1}{x^2}\,v^{3/2}\left(1+.0247\sqrt{\frac{T}{V}}\right) \tag{7}$$

where V is the applied potential in volts, x the sheath thickness in cm, I the current density in amperes/cm², M the molecular weight of the ions, and T the absolute temperature.

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[7] Langmuir, G. E. Rev. **27**, 544 (1924).

If we take $I=100$, $V=15$, approximately the cathode drop for copper, $M=63.5$, and $T=6000°$, we find for the sheath thickness,

$$x=7.7\times10^{-4}\text{ cm}\ . \tag{8}$$

Within this sheath it is not necessary for the gas to be thermally ionized, but at the edge of the sheath the random positive ion current must have the full value of 100 amperes per cm². The vapor then must have a temperature of 6000° within 7.7×10^{-4} cm from the cathode.

Since this separation from the cathode of 7.7×10^{-4} cm is comparable with the mean free path in the gas at 6000°, the rate of heat flow across the space into the cathode can not be calculated from the thermal conductivity of the vapor in bulk, but an upper limit to this heat flow may be determined from the kinetic theory. If we assume that all the molecules which enter the positive ion sheath reach the cathode and there give up all the energy which they have in excess of that corresponding to the cathode temperature, the heat thus calculated as given up to the cathode will be in error by being too large, inasmuch as collisions with molecules of gas in the positive ion sheath, and partially elastic collisions with the cathode are not allowed for. Letting n_1 be the number of molecules per cm³ at temperature T at the edge of the sheath remote from the cathode, the number of molecules which reach the cathode per second will be approximately

$$n_2=\tfrac{1}{4}n_1v_1 \tag{9}$$

v_1 being the mean translational velocity of the molecules, and since each molecule gives up the energy $3/2k(T-T_0)$, T_0 being the temperature of the cathode, we have as an upper limit for the heat lost to the cathode per second,

$$W=\tfrac{3}{8}n_1v_1k(T-T_0) \tag{10}$$

Letting $n_1=7.38\times10^{21}$, $v_1=1.14\times10^3T^{1/2}$ (copper), $k=1.37\times10^{-16}$, $T=6000°$, $T_0=2580°$ (boiling point of copper) we have in watts

$$W=1770\text{ watts} \tag{11}$$

If the cathode drop is 15 volts and the current density is 100 amperes per cm², the electrical input is 1500 watts. A large part, very likely the larger part, of this electrical input is communicated by bombarding positive ions directly to the cathode as heat, but not all of it, inasmuch as many of these positive ions will be reflected with a large part of their oncoming velocity, and many will collide with gas molecules in the space of 7.7×10^{-4} cm of Eq. (8). Now remembering that (11) is much too high for reasons given, we see that the electrical input is quite sufficient to make up for the heat lost to the cathode.

CONCLUSION AND SUMMARY

The theory of thermal ionization in the electric arc, as advanced by Compton to explain the conductivity in the positive column, can also account for the passage of current to the cathode without requiring thermionic emission from the cathode. Calculations made for the copper arc, using equations of Langmuir and Saha, show that with a reasonable assumption of temperature of the vapor, the ionization is sufficient for the positive ions to carry the whole current to the cathode. The heat lost to the cathode by the hot vapor is of such an order that it can be made up for by the electrical input at the cathode.

A hot cathode is therefore not necessary for an arc. High temperature appears to be essential, but it may be in the gas immediately adjacent to the cathode, and need not be in the cathode itself.

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December 2, 1925.

APRIL, 1926 PHYSICAL REVIEW VOLUME 27

SECONDARY ELECTRONS FROM IRON

By H. E. Farnsworth

Abstract

Secondary electron emission from iron as a function of energy of primary electrons, 0 to 300 volts.—Curves showing ratio of secondary to primary electron current as a function of primary velocity were obtained with three forms of apparatus. Two have been previously described. The limiting curves obtained after red-heat treatment of samples of electrolytic Fe having very large crystals, and of chemically pure Fe obtained from Kahlbaum were similar to those obtained for a film of Fe deposited by evaporation. The curves all have sharp maxima at 1.2 and 7.0 volts with minima at 3.7 and 12.0 volts, and a less prominent maximum and minimum at 10.0 and 9.0 volts, respectively. Of several metals tried, Fe is the only one, in addition to Cu, for which such sharp maxima and minima have been obtained. Potentials corresponding to positions of the maxima are interpreted as critical potentials. A steady upward trend of the curve begins at 12.0 volts, which is interpreted as being due to ionized electrons. Slight changes in slope of the curve at higher potentials were observed but these varied with conditions, and hence are taken to have no real significance.

Evidence of structure of evaporated Fe film.—While previous results for Cu indicate that a layer deposited by evaporation is amorphous, the present results indicate that a similarly formed layer of Fe is crystalline.

I. Introduction

A STUDY of secondary electrons produced when various metals, namely Ni, Cu, Ag, W, Pt, Pd, Mg, and Al, are bombarded by electrons varying in velocity from 0 to 250 volts has previously been described.[1,2] The study consisted first, in obtaining the number of secondary electrons as a function (1) of the primary velocity, (2) of the previous heat treatment of the metal, and (3), in the case of Cu, of the surface structure of the metal; second, in obtaining the velocity distribution of the secondary electrons for any given primary velocity.

In the case of all the metals investigated, a marked change in the magnitude of the secondary electron current, as well as in the shape of the secondary electron curve (curve showing secondary current as a function of primary velocity), was produced by heating the metals at red heat. The secondary current decreased with heat treatment for all metals tried, except Al and Mg for which it increased. A limiting curve for each metal was obtained after heating at red heat for some minutes. The changes in shapes of the secondary electron curves con-

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[1] H. E. Farnsworth, Phys. Rev. **20**, 358 (1922).

[2] H. E. Farnsworth, Phys. Rev. **25**, 41 (1925).

sisted in the appearance of various breaks in the region of low velocities, 0 to 30 volts, but for no metal were these changes found to be so noticeable as they were for Cu. For this metal, four distinct maxima and four minima appeared in the region 0 to 30 volts, subsequent to red-heat treatment of the target. Further experiments on Cu showed that heat treatment produces two separate results: (1) outgassing of the metal, the rate of which varies with temperature, (2) removal of an amorphous surface layer, thus exposing the crystalline structure beneath, or the transformation of this amorphous layer into crystalline form. The second result occurred at a very critical temperature (dull red heat) in less than one minute. This change was detected by the sudden appearance of the several maxima and minima in the secondary electron curve, while previous heating at a slightly lower temperature for some time was only effective in lowering the curve without changing its shape—a result of outgassing.

Since the other metals were studied previous to the above observation, the above two effects were not separated, although they undoubtedly exist. No direct reason could be found as to why Cu is the only one of the investigated metals upon which heat-treatment produced such a marked effect, except that visible surface crystals of Cu are the most easily produced. Hence, it might be expected that other substances upon which prominent surface crystals are formed would show effects similar to Cu. To investigate this point the secondary electrons from Fe were studied. Fe was chosen because some very crystalline electrolytic Fe was available from Professor Terry.

The existence of several critical potentials, in the region 0 to 200 volts, at which the secondary electron current from Fe suddenly increases has been reported by Stuhlman.[3] These have been attributed to the photoelectric action of soft x-rays that are caused by electronic bombardment of the metal surface. More recently Petry[4] has obtained many slight changes in slope of the secondary electron curves for Fe, Ni, and Mo in the region zero to several hundred volts which, in the case of the higher potentials, do not appear to be due to the above cause. In the present experiments on Fe, special effort was made to obtain evidence of the existence of such critical potentials by taking observations at smaller voltage intervals than previously in the higher velocity region.

As reported in a previous article,[2] attempts were made to obtain velocity distribution curves of secondary electrons from Cu which would indicate the existence of inelastic collisions at critical voltages corresponding to the position of the maxima in the secondary electron curves. Although some indication of such inelastic collisions was found, the results were not entirely satisfactory, so further investigation is described in the present paper.

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[3] Stuhlman, Science **56**, 344 (1922); Phys. Rev. **25**, 234 (1925).

[4] Petry, Phys. Rev. **26**, 346 (1925).

II. Apparatus and Procedure

As formerly described, two different forms of apparatus were used for study of Cu. The first, which was suitable for measuring only the ratio of the secondary to the primary current as a function of the primary velocity, consisted of a series of insulated molybdenum cylinders and diaphrams. The target to be studied was alternately interposed and withdrawn in front of a Faraday cylinder (Fig. 2, loc. cit.[2]). The second, which was designed for the purpose of obtaining an accurate measure of the velocity distribution of secondary electrons for any given primary velocity, consisted essentially of a conducting sphere at whose center the small target to be studied could be placed (Fig. 3, loc. cit.[2]). A nearly radial retarding field for secondary electrons could be applied between sphere and target so as to effect an accurate measure of the velocity distribution of secondary electrons. Although this apparatus was intended only for observations on velocity distribution of secondary electrons, it was found that results on the ratio of secondary to primary current for Cu agreed with those of a previously used apparatus, so that this apparatus was used to extend the investigation to Fe. As previously mentioned, it was necessary to keep the potential of the cylinder *C* (Fig. 3 loc. cit.[2]), which limits the primary beam, about 3 volts positive with respect to the sphere in order to keep the primary beam from spreading before reaching the target. While studying an Fe target it was found impossible to give *C* a potential for low primary velocities, which would prevent spreading of the primary beam. From the nature of the measurements, a spreading of the primary beam, so that some of it misses the target and strikes the sphere, results in an effective increase in the secondary current which cannot be separated from the true secondary current. Hence, the curve obtained was much higher than the correct one in the region of low velocities, the height varying with the potential of *C*. This effect was negligible for primary velocities higher than about 10 volts. In order to obtain the correct curve in the region below 10 volts, the apparatus shown in Fig. 2 (loc. cit.[2]) was used. By means of this apparatus the effect of scattering could be eliminated. It was at first thought that this scattering was due to the magnetic property of the iron target, but investigation indicated that it was independent of the position of the target and occurred very near the opening in the sphere where the primary electrons enter, and that all of those electrons which are scattered suffer a very great change in direction, there being no electrons which are scattered through only a few degrees. These scattered electrons are probably the ones which pass close to the edges of the diaphram.

Since this scattering would change with the retarding potential of the sphere, it is obvious that it would seriously affect the results on velocity distribution of secondary electrons. In an attempt to eliminate this difficulty, the apparatus was modified as shown in Fig. 1 of the present paper. It is the same as that described on p. 46–47 of the above reference,[2] except for the addition of a Faraday cylinder *E* surrounded by a co-axial cylindrical metallic shield *G*, both constructed of copper. The position of the cylinders is as shown, with the forward ends at the center of the sphere. The shield was held in place and also insulated from the Faraday cylinder by three quartz rods of 1 mm diameter and 7 cm length. The rods were placed symmetrically and parallel to the axes of the cylinders and were held in place by small projections on the inner cylinder. The difference in diameters of the cylinders was just sufficient to insure a snug fit after inserting the quartz rods. The Faraday cylinder was fastened to and held in position by two glass rods (not shown in Fig. 1) upon which the target-mounting slid, so that the target could be moved along the axis of the cylinders, the plane of the target being perpendicular to the axis. Circular openings in the ends of the cylinders were just large enough to permit the free passage of the target. The target could thus be placed in the forward position, flush with the end of the cylindrical shield, or withdrawn (by means of a magnetic control) into the side-tube

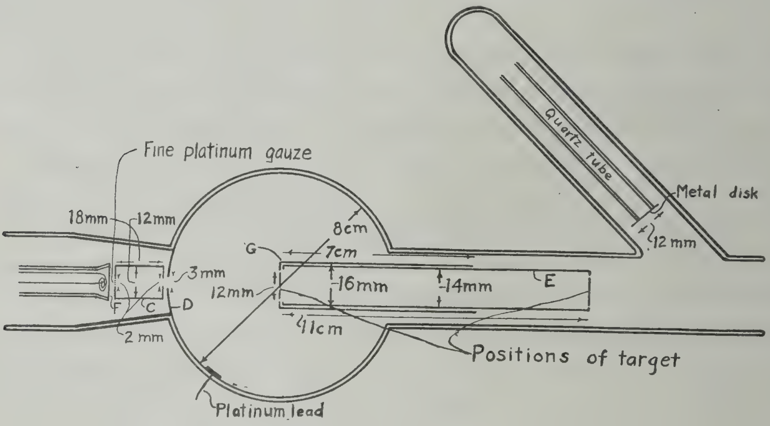

Fig. 1. Apparatus.

where it could be heated at red heat by high-frequency induction. The Faraday cylinder and target were kept connected at all times. The presence of the shield prevented any electrons from reaching the Faraday cylinder by multiple reflection from the sphere or by scattering.

The procedure was then to measure (1) the current to the target when in the forward position, (2) the total or primary current to the Faraday cylinder and target with the latter at the back end of the cylinder, this being a measure of the total current striking the target since no electrons could escape from the cylinder.[5] Subtracting the first current from the second then gives the secondary current. The ratio of this secondary current to the primary current, as a function of the retarding potential on the sphere, should then give a measure of the velocity distribution of secondary electrons for any given primary velocity. The secondary electron curve can also be obtained by taking the ratio of secondary to primary current as a function of primary velocity, the potential of the sphere being constant and equal to that of the target. This procedure differs from that used with apparatus shown in Fig. 3 of above reference,[2] in the method of measuring the total current. Any scattering of the primary electrons on entering the sphere S will not influence the measurement of the ratio of secondary to primary current provided that this scattering remains the same for these two observations at any particular primary velocity. Thus the results should not be affected by this change even if the scattering changes with the primary velocity or with the potential of the sphere.

Conditions previously described regarding vacuum were obtained in the present experiments. In addition a charcoal tube was attached to the present apparatus and immersed in liquid air. This, however, did not change the results. Helmholtz coils were used to compensate the earth's magnetic field.

III. Results

A. Results on ratio of secondary to primary current, as a function of primary velocity, for Fe are shown in Fig. 2. Curve 1 is the limiting curve for an Fe target obtained after red-heat treatment. The form of the curve in the lower region, below about 13 volts, was found to be the same for two specimens of Fe—a very crystalline electrolytic Fe and a chemically pure Fe obtained from Kahlbaum—after red-heat treatment. It was also obtained with three different forms of apparatus: that shown in Fig. 1 of the present paper, and those of

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[5] Measurements of current to the cylinder and target for various positions of the target showed that the cylinder was longer than necessary to be completely absorbing.

Figs. 2 and 3 of above reference.[2] The agreement was in all cases very close except in the one referred to above which was affected by scattering.

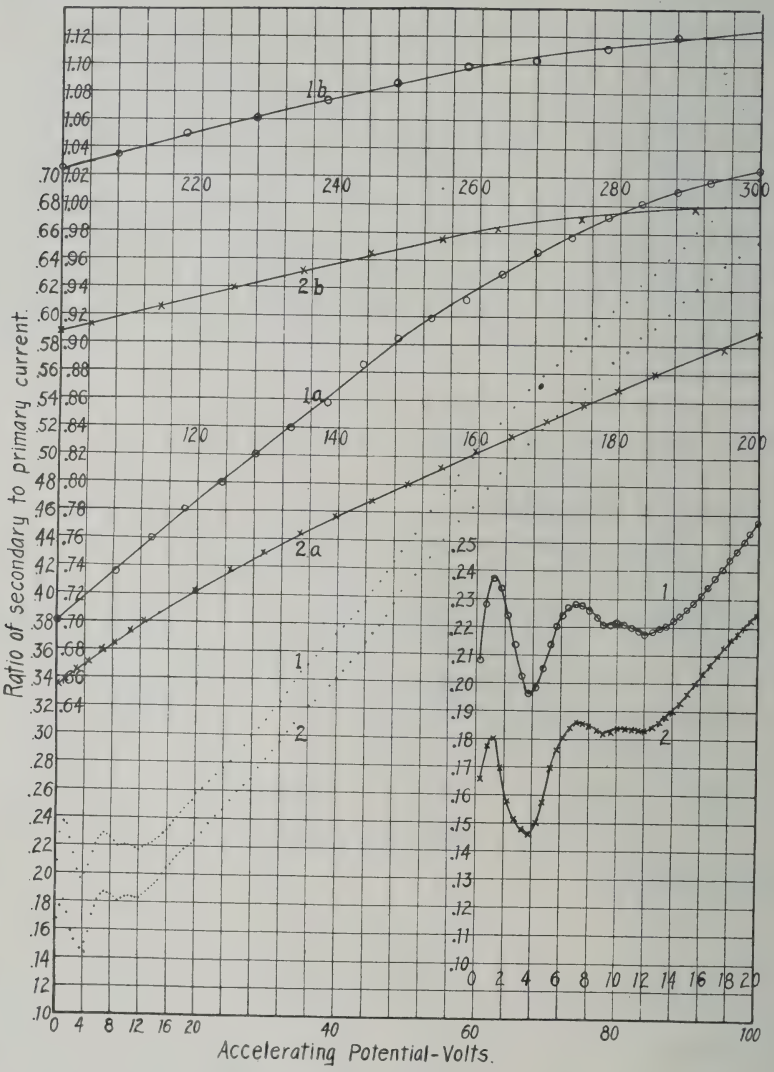

Fig. 2. Secondary electron curves. 1 is for Fe after red-heat treatment. 2 is for a film of Fe deposited by evaporation. 1a and 2a are extensions of 1 and 2, respectively, from 100 to 200 volts and are plotted to the upper scale of ordinates. 1b and 2b are extensions of 1a and 2a, respectively, from 200 to 300 volts. The inset is a magnified portion of curves 1 and 2.

It is seen that there are sharp maxima at 1.2 and 7.0 volts with minima at 3.7 and 12.0 volts and a less prominent maximum and minimum at

10.0 and 9.0 volts,[6] respectively, with a steady upward trend beginning at 12 volts. In the region above about 13 volts there are several slight changes in slope noticeable. Although the general trend of the curve in this region was similar in all of the above mentioned cases, the positions of the slight changes in slope were found to vary with uncontrollable conditions as well as with the form of apparatus and the particular target used. It may be mentioned, however, that of the curves obtained, it is possible to select a large number which agree fairly well with curve 1 in the positions of these slight changes in slope but this procedure has no justification. The disagreement in the position of these slight breaks does not appear to be due to errors in observation since it was possible to accurately repeat a set of observations within a short time after they were taken.

The effect of outgassing was to decrease the secondary current as in the case of most of the other metals previously investigated. The curve obtained subsequent to baking at 400°C but previous to red-heat treatment was a smooth curve without maxima and minima and higher than curve 1.

Curve 2 is for a film of Fe deposited by evaporation and is seen to be lower than curve 1 but agrees with it in the position of the maxima and minima.

Correction has been made in these curves for contact potential between source and target and for change in potential of target due to heating, as described in a previous paper (loc. cit.[2]).

B. *Velocity distribution of secondary electrons from Fe.* Although the apparatus shown in Fig. 1 was designed to give a more accurate measure of velocity distribution than that previously obtained, an unanticipated difficulty was encountered when attempting to effect these measurements. The number of electrons entering the Faraday cylinder, with the target withdrawn to the far end, was found to be equal to the number which struck the target when in the forward position, only when the potential of the sphere was equal to that of the cylinder and target. As the potential of the sphere was made negative with respect to the target and cylinder, the number of electrons which entered the Faraday cylinder, with the target back, became less than the number striking the target when in the forward position, the difference going to the shield instead of to the Faraday cylinder. This spreading of the primary beam at the opening of the Faraday cylinder was obviously caused by the distorted field which resulted when the target was withdrawn. This distortion increased as the retarding potential on the sphere was increased so that the condition necessary for the measurement of velocity distribution of secondary electrons effected circumstances which made this measurement impossible. Preliminary measurements with the apparatus before the Faraday cylinder was inserted were sufficient to show that, in general, the velocity distribution of secondary electrons from Fe is similar to that of other metals, i.e. the number of low-velocity secondary electrons increases as the primary velocity increases but these results are not accurate enough to decide the existence or non-existence of the effect in question.

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[6] The maximum at 10 volts was in many cases not as noticeable as in the curve shown. In some curves there was no actual maximum but a region of the curve separated from the rest by changes in slope at 9.0 and 12.0 volts.

IV. Discussion

The fact that the same type of secondary electron curve was obtained for two different specimens of Fe and with three different forms of apparatus is sufficient evidence of the validity of this curve. The occurrence of sharp maxima and minima at certain critical potentials in the low-velocity region of the above curve for Fe shows the existence of a phenomenon which has an effect on the secondary electron curve as noticeable as that observed in the case of Cu.

In the previous report on Cu it was shown that if one makes certain simple assumptions regarding inelastic collisions a curve containing maxima and minima is obtained which approximates closely to the experimental curve, at least in the region of lower velocities. The maxima occur at certain critical potentials followed by minima. If the work function of the metal is taken into account, as noted by Petry,[4] all primary electrons strike with energy due to the accelerating potential plus that acquired in falling through the surface and all secondary electrons with energy less than that corresponding to the work function will be unable to escape.[8] Hence an interval equal to at least the work function in volts might be expected to separate a maximum from the minimum following it. This interval, however, would depend on the type of critical potential. For an ionization potential it would depend on the distribution of the residual energy between the two colliding electrons after impact. If the energies of the two electrons are equal, the interval referred to above should be twice the work function. If either of the electrons has all of the residual energy after impact, the interval should be equal to the work function. In the case of a resonance posential it would also be equal to the work function. Referring to the present results on Fe, the difference between the maximum at 7.0 volts and the minimum at 12.0 volts is the same as the work function ascribed to Fe by Thomas.[7] There is, however, a slight minimum and maximum between these two values. The difference between the first sharp maximum at 1.2 and minimum at 3.7 volts is seen to be only one-half of the above work function of Fe. It therefore seems necessary to conclude either that the work function of Fe is less than 5 volts or that some such condition as the following exists: that the energy loss at the first inelastic collision is only equivalent to 3.7 volts but the probability of its occurrence is negligible until an actual accelerating potential of 1.2+5.0 volts is reached. (Eldridge[9] has shown that a similar idea is necessary to explain the 6.7 resonance potential of Hg vapor.) The residual energy of 2.5 volts is not sufficient to allow the election to escape through the surface so that the secondary current begins to decrease at this point. When the primary electron has energy of 3.7+5.0 volts, after falling through the surface layer, it loses 3.7 volts on collision and has 5.0 volts left which will just allow it to emerge through the surface. Thus the secondary current begins to increase at this point. A knowledge of the velocity distribution of secondary electrons should throw light on this question. At any rate, the gradual rise in the curve beginning at 12.0 volts is undoubtedly due to electrons resulting from ionization. It may be noted that Petry's[4] curve for Fe shows a maximum at about 7 volts with a minimum at about 10 volts.

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[8] From this point of view it is evident that the effect of critical potentials of solids having a value smaller than the work function cannot be observed at primary velocities corresponding to the critical potential, since the slowest primary electron has an energy equal to the work function.

In the study of Cu it was found that excessive heating of the target near the melting-point resulted in a smoothing out of the various maxima and minima, which was attributed to a change in crystal structure. No such effect was observed for Fe, which would indicate that the crystal structure of Fe is more stable than that of Cu.

The curve for evaporated Fe (curve 2, Fig. 2) is seen to be similar in form to curve 1, at least in the region of low velocities. Previous results show that depositing an evaporated Cu film onto a Cu target causes the disappearance of the sharp maxima and minima—a result which suggests that evaporated Cu is amorphous. The similarity of curves 1 and 2 for Fe then indicates that evaporated Fe is not amorphous but crystalline, the difference in absolute values indicating that evaporated Fe is more gas-free than the other.

Although the present results prove the existence of critical potentials for Fe in the region below about 13 volts accelerating potential, there appears to be no true critical potentials for higher accelerating potentials.

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[7] C. H. Thomas, Phys. Rev. **25,** 331 (1925).

[9] J. A. Eldridge, Phys. Rev. **20,** 459 (1922).

Since this article was first written, two papers by A. Becker[10] have appeared on velocity of secondary electrons from Pt covered with lampblack and from pure platinum. They, however, contain nothing immediately related to the present results.

These experiments were performed at the University of Wisconsin during the past summer and the writer expresses his appreciation to Professor C. E. Mendenhall for the privilege of continuing the investigation in that laboratory.

UNIVERSITY OF MAINE,
ORONO, MAINE.
November 10, 1925.

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[10] A. Becker, Ann. d. Physik **78,** 228 (Nov. 1925); **78,** 253 (Nov. 1925).

THE RESONANCE POTENTIALS OF HELIUM AND DOUBLE IMPACTS BY ELECTRONS IN HELIUM

By George Glockler*

Abstract

First and second critical potentials in helium.—A tube with five platinum electrodes was used to determine the first two critical potentials in carefully purified helium. The *inelastic impact method of Franck* was used over a pressure range from 0.13 to 13.00 mm and gave values of 19.87 ± 0.06 for the first, and 20.62 ± 0.06 volts for the second critical potential. The *method of Lenard* for pressures from 0.96 to 2.85 mm gave values of 19.83 ± 0.02 and 20.57 ± 0.06 volts. The spectroscopic value corresponding to the transition $1S \rightarrow 2s$ (A) is 19.77 volts and that corresponding to $1S \rightarrow 2S$ (B) is 20.55 volts. The observed difference between first and second critical potentials, 0.75 (Franck method), 0.74 volts (Lenard method), is in excellent agreement with the spectroscopic value of the difference $B-A$, 0.78 volts. The average *initial velocity correction* was determined by two different methods which led to concordant results.

Critical potentials in helium due to double impact.—Three critical potentials in helium near 40 volts were observed by the Franck method. The values are 39.62, 40.47 and 40.96 ± 0.04 volts, the last being the most prominent. The spectroscopic values for double impacts are 39.54 volts ($1S \rightarrow 2s$ and $1S \rightarrow 2s$), 40.32 volts ($1S \rightarrow 2s$ and $1S \rightarrow 2S$), and 40.89 volts ($1S \rightarrow 2s$ and $1S \rightarrow 2P$). The observed difference between the first critical potential and the most prominent double impact point is 21.09 volts, in excellent agreement with the spectroscopic value of the transition $1S \rightarrow 2P$, 21.12 volts.

SEVERAL experimental determinations of the critical potential of helium have been made by the method of electron impact.[1] Franck[2] has cleared up the situation regarding interpretation on the basis of Lyman's spectroscopic measurements[3] and at present it is accepted that the first critical potential of helium at 19.77 volts corresponds to a transition ($1S \rightarrow 2s$) from the normal to a metastable state.

In determining the critical potential of a gas by the method of electron impact a correction has to be made for the velocity distribution of the electrons, their initial velocity and for the contact potential difference between the filament and the other electrodes. In addition the efficiency of impact must be considered as shown by Sponer[4] and Dymond.[5] Franck and Knipping[6] determined the last two corrections in the case of helium by measuring the volt-difference between the kinks in a current-potential curve corresponding to a single impact (type $A = 1S \rightarrow 2s$) and a double impact (type $A = 1S \rightarrow 2s$ and type $B = 1S \rightarrow 2S$). However, Dymond[5] has shown that in his experiments this difference is not 20.55 volts, but 20.9 volts, and he accordingly assumes that the double impact must be of the type BB. In this investigation the two single impacts appear as usual. The double impact that is most prominent occurs at 40.96 volts (corrected) and the difference between this point and the first drop is 21.09 volts corresponding in magnitude to the transition $1S \rightarrow 2P$. Indications were obtained at higher pressures which tend to show that the other types of double impact AA and AB also can occur.

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* National Research Fellow in Chemistry.

[1] K. T. Compton and F. L. Mohler, Bull. Nat. Res. Council, No. 48, p. 85 (1924).

[2] Franck, Zeits. f. Physik, **11,** 155 (1922).

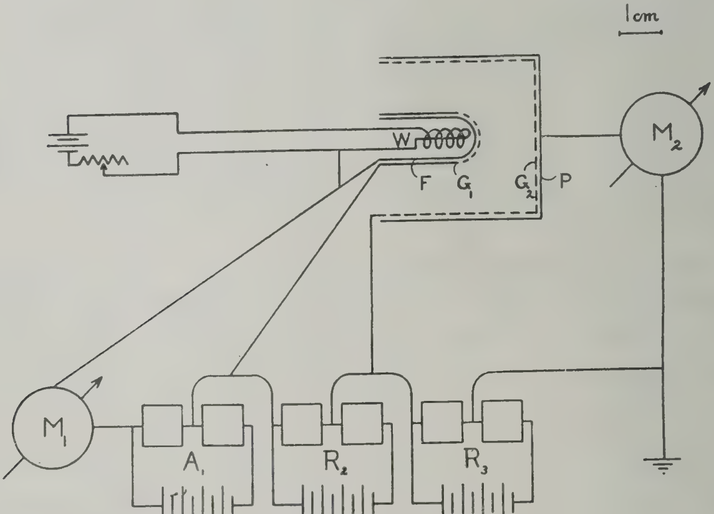
[3] Lyman, Science, **56,** 167 (1922).

[4] Sponer, Zeits. f. Physik, **7,** 185 (1921).

[5] Dymond, Proc. Roy. Soc., **A107,** 291 (1925).

Experimental Procedure

The five-electrode tube used is shown in Fig. 1. All electrodes are of platinum. The gauzes G_1 and G_2 are 52 mesh/inch and the wire is 0.004 inch thick. W is a tungsten filament that heated the calcium oxide covered platinum thimble F by radiation. F is an equipotential surface. Between F and gauze G_1 an accelerating field is applied by means of the potentiometer A_1 of 10,000 ohms. M_1 is a galvanometer that measures the total emission from F. This total current was kept constant by regulating the external resistance in the heating circuit. M_2 is a galvanometer of 50,000 megohms sensitivity (880 ohms resistance) and is used



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[6] Franck and Knipping, Zeits. f. Physik, **1**, 320 (1920).

at a scale distance of 3 meters. Both galvanometers were read on the same scale by means of two telescopes.

The helium was purified by sparking with a little added oxygen for 24 hours and then it was passed through a quartz tube containing magnesium ribbon, copper shavings, and granular copper oxide at 550°C, thus removing nitrogen, oxygen, and hydrogen. It was further purified by passing through a trap containing cocoanut charcoal immersed in liquid air and stored over phosphorus pentoxide. It was admitted into the experimental tube by means of a mercury trap so that no stopcocks were used at any place in the vacuum system. The pressures were read on a McLeod gauge. The voltages on the potentiometer were measured by means of a standard cell before and after each run. Readings were taken in steps of 20 ohms which corresponds to about 0.1 volt, since the battery supplying the potentiometer was 50 volts. Liquid air was kept on a trap to remove mercury vapor, except in the experiments using the Lenard method.

THE EXPERIMENTAL RESULTS

1. *The Franck method.* The current potential curves were obtained by two methods. The first of these was the inelastic impact method of Franck, in which the drop in electron current reaching the plate was determined as a function of the first accelerating field. No retarding

TABLE I

Franck method

Run	Press. mm Hg	Total drop across potentiometer		Peaks of difference curves First		Second		Third		Filament	
		before	after	ohms	volts	ohms	volts	ohms	volts	volts	amps.
0	0.13	34.06	34.06	.....	.....	....	.....			4.30	4.40
1	.81	34.06	34.06	6220	21.18	6410	21.82			5.00	5.40
2	.81	34.06	34.06	6226	21.20	6410	21.82			4.90	5.30
3	.83	34.06	34.06	6190	21.11	....	.....			4.80	5.25
4	.83	34.06	34.06	6202	21.12	6450	21.97			5.00	5.70
5	3.35	34.06	34.06	6218	21.18	....	.....			5.25	5.75
6	0.75	50.72	50.72	4130	20.93	4310	21.86			4.80	5.30
7	2.63	50.72	50.72	4170	21.15	....	.....	8320	42.19	5.50	6.50
8	5.50	50.84	50.84	4166	21.18	....	.....	8310	42.25	5.80	7.00
9	5.50	50.72	50.71	4158	21.10	....	.....	8330	42.25	5.80	7.20
10	5.50	50.72	50.72	4164	21.12	....	.....	8330	42.25	5.70	6.70
11	1.01	50.78	50.66	4166	21.13	4350	22.06	....	.....	4.80	6.10
12	1.83	50.64	50.63	4186	21.19	....	.....	8350	42.28	5.00	5.80
13	2.91	51.32	51.29	4183	21.23	....	.....	8240	42.27	5.25	6.25
14	3.70	51.17	51.13	4142	21.20	....	.....	8260	42.25	5.50	6.50
15	5.00	51.11	51.10	4122	21.06	....	.....	8260	42.20	5.60	6.75
16	13.00	50.97	50.96	4134	21.07	....	.....	8270	42.15	6.20	7.70
				Average values	21.14		21.89		42.23		
				Average deviation	±.06		±.07		±.04		

field was applied between the second grid and the plate. The experimental curves obtained by this method are shown in Fig. 2 (*B* and *D*) in which galvanometer readings are plotted against potentiometer resistance.

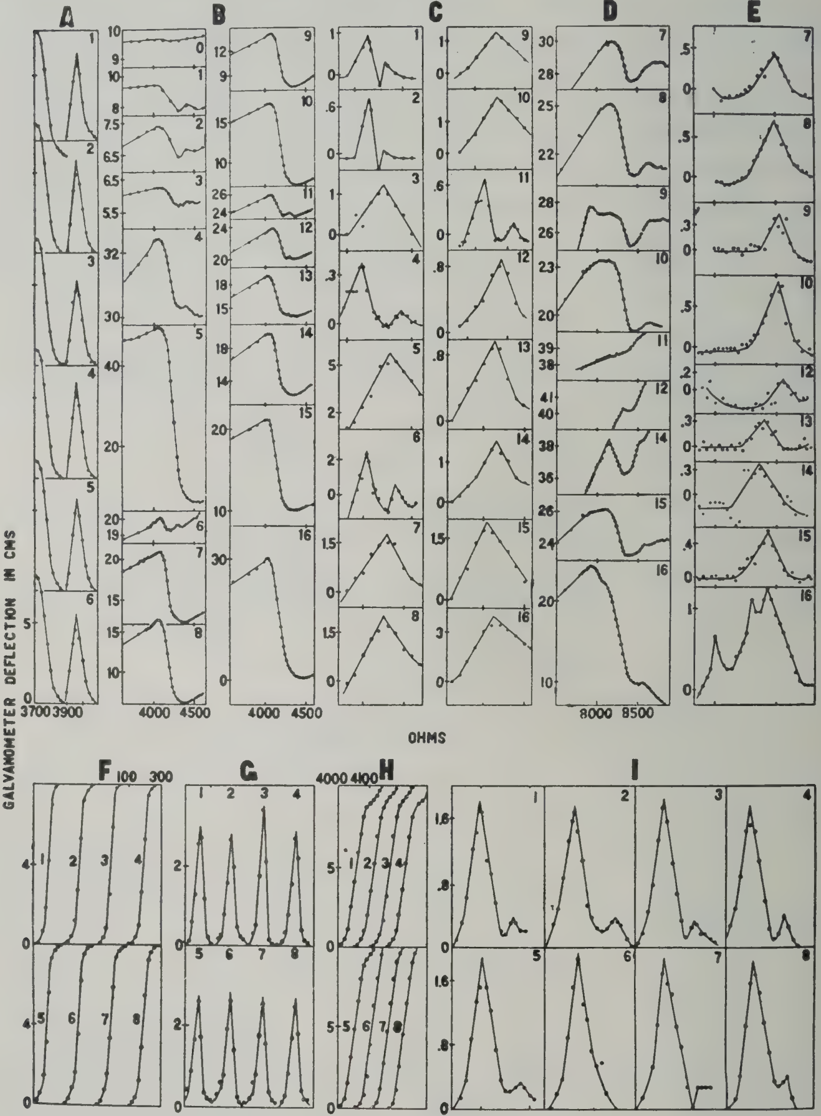

Fig. 2. Experimental current-potential curves.

These curves were then differentiated by taking the difference between successive galvanometer readings and replotting against potentiometer resistance. These difference-curves are shown in Fig. 2 (*C* and *E*). The maxima of the difference-curves correspond to the points where *most* of the electrons from the filament have obtained enough energy to resonate. For the measurements in the neighborhood of 20 volts, the voltages corresponding to the maxima for the first current-drop are given in Table I, column 6, and for the second drop in Table I, column 8.

Measurements in the neighborhood of 40 volts were also made in the last eight experiments, and the peaks obtained are shown in Fig. 2 (*D* and *E*), and given in Table I, column 10.

The initial velocity correction (*Method I*). This correction was determined in a vacuum by applying a constant accelerating field (A_1) between F and G_1 of about 20 volts and by noting the decrease in plate-current as the retarding field (R_2) between G_1 and G_2 was increased. The correction is negative due to a contact potential between F and G_1.

If P_c is this contact potential and V_i is the actual velocity with which the electrons leave the filament, then a given electron can just reach the plate when

$$A_1+V_i+P_c=R_2 \tag{1}$$

where A_1 and R_2 are the accelerating and retarding fields respectively.

The results obtained are shown in Fig. 2 (*A*), where both the experimental curves and the difference curves are given, the latter being displaced to the right. In these curves galvanometer readings are plotted against the resistance, which gives the retarding field. It will be seen that the *first* drop in current due to R_2 occurs at 3700 ohms (=18.80 volts). This initial drop must be due to the slowest electrons. If they leave the filament with zero velocity, then

$$A_1+P_c=R_2 \tag{2}$$

and the contact potential is found to be acting as a retarding potential (i.e., $P_c=-1.6$ volts).

TABLE II

Data for determination of initial velocity correction (*pressure* 10^{-5}*mm*Hg)

Run	Total voltage first field A_1		Total voltage second field R_2		Field A_1		Field R_2 at peak		Correction	Filament	
	before	after	before	after	ohms	volts	ohms	volts	R_2-A_1	amps	volts
1	50.66	50.66	50.41	50.41	4000	20.26	3770	19.00	−1.26	3.70	4.70
2	50.80	50.66	50.48	50.37	"	20.29	"	19.01	−1.28	3.70	4.75
3	51.39	51.35	51.19	51.17	"	20.56	"	19.30	−1.26	3.80	4.00
4	51.29	51.26	51.11	51.09	"	20.51	"	19.26	−1.25	3.70	3.80
5	51.18	51.19	50.99	51.01	"	20.47	3760	19.18	−1.29	3.75	3.85
6	50.98	50.97	50.80	50.79	"	20.38	"	19.10	−1.28	3.75	3.90
					Average correction				−1.27 volts		

The velocity distribution was thus determined with no gas in the tube. It might be thought that the distribution is different with helium present. However, the critical points should then show some trend with pressure. No such trend was observed. Of course the presence of the gas necessitates a greater heating current in the tungsten filament W as a good deal of heat is conducted away by the gas.

From the difference-curves the average correction was determined. The results are given in Table II.

2. *The Lenard method.* In the second method, Lenard curves were taken with a constant large retarding field (30 volts) between the second gauze G_2 and the plate. The results are shown in Fig. 2 (H and I) and they are summarized in Table III.

TABLE III

Lenard method

Run	Press. mm Hg	Total drop		Peaks of diff.–curves First		Peaks of diff.–curves Second		Filament		Liq. air	Diff.–curve peaks for correction	
		before	after	ohms	volts	ohms	volts	amp	volts		ohms	volts
1	1.08	50.78	50.78	4102	20.82	4240	21.53	5.45	5.50	off	202	1.02
2	1.21	50.71	50.71	4112	20.85	4284	21.71	5.60	6.00	"	194	0.98
3	1.36	50.69	50.69	4114	20.85	4246	21.52	5.65	6.05	"	206	1.04
4	0.96	50.61	50.61	4108	20.79	4250	21.51	5.43	5.75	"	198	1.00
5	1.21	50.60	50.60	4118	20.84	4280	21.61	5.55	6.00	"	196	0.99
6	2.85	50.60	50.60	4118	20.84	....	.....	6.07	6.62	"	194	.98
7	1.14	50.50	50.50	4122	20.82	....	.....	5.60	6.10	on	194	.98
8	1.15	50.48	50.48	4124	20.82	4270	21.55	5.55	6.00	"	193	.98
		Average values			20.83		21.57					1.00
		Average deviation			± .02		± .06					± .02

The total rise in positive current was about 9 cm on the galvanometer scale in runs Nos. 1 to 5. In run 6 the total rise was 17 cm. However, the two last runs were made with liquid air on the charcoal so as to remove mercury vapor and the total rise was only 3 cm, showing that most of the current was probably due to positive ions of mercury produced by the metastable helium atoms.

The initial velocity correction (*Method II*). Before the Lenard experiments could be made the filament had to be recoated with calcium oxide as its emission had decreased. The correction for the recoated filament was determined by Method I as described above and Method II as described below. Both gave identical results.

In Method II, instead of making separate experiments in a vacuum with two fields, the correction was now determined with gas in the tube at the same pressure as was to be used in the Lenard experiment immediately following. The increase in electron current to the plate was measured as the first accelerating field was increased from 0.5 volt to 1.5 volts while the other fields were zero. After such an experiment the retarding field (R_3) between G_2 and the plate was applied and a Lenard experiment was performed.

The correction for the recoated filament amounted to -1.00 volt, while previously it was -1.27 volts. The difference is presumably due to a change in contact-potential. It is important then to measure the correction for each filament and to make sure that it does not change.

The results are shown in Fig. 2 (*F* and *G*) and the last column of Table III. The figures given are the voltages A_1 which have to be applied in order to get the "average" electron to come through grid G_1 with approximately zero velocity and hence the correction has to be subtracted from the value of A_1 found in the later Lenard experiments. A few measurements of the correction were also made by Method I on the new filament and gave concordant results.

SUMMARY OF RESULTS

When the proper corrections as described above are applied to the critical points, the values given in Table IV are obtained.

TABLE IV

Type	Transitions	Volts Spectroscopic	 Franck method	 Lenard method	Peak No.
A	$1S\rightarrow 2s$	19.77	19.87 ± 0.06	19.83 ± 0.02	1
B	$1S\rightarrow 2S$	20.55	$20.62\pm .06$	$20.57\pm .06$	2
AA	$1S\rightarrow 2s$ and $1S\rightarrow 2s$	39.54	39.62	....	3
AB	$1S\rightarrow 2s$ and $1S\rightarrow 2S$	40.32	40.47	....	4
AC	$1S\rightarrow 2s$ and $1S\rightarrow 2P$	40.89	$40.96\pm .04$	....	5
BB	$1S\rightarrow 2S$ and $1S\rightarrow 2S$	41.10	....	....	
BC	$1S\rightarrow 2S$ and $1S\rightarrow 2P$	41.67			

These values depend on the corrections applied. However, the differences between the peaks are independent of the initial velocity correction and the following quantities are obtained.

TABLE V

Transition	Spectroscopic	Franck method	Lenard method
$B-A$	0.78 volts	0.75 volts	0.74 volts
$AC-A$	21.12	21.09	....

DISCUSSION OF RESULTS

It is seen that at a pressure of 0.13 mm (Fig. 2 *B*, Run *O*) no drop in current was obtained. At this pressure the mean free path of the electron (0.96 cm) is nearly as great as the distance between the gauzes (1.1 cm). At a pressure of 1 mm the m.f.p. of the electron is 1.25 mm, while the distance between the filament and grid G_1 is 0.5 mm. In some of the experiments the pressure was so high that some of the electrons must have made impacts in the region between filament and grid G_1. However, the voltages at which the maximum occurs do not seem to be different.

In the Franck method a small retarding field of 0.34 volt between the plate P and grid G_2 was employed in runs 1 to 5, but no retarding field was used in the later experiments. Nevertheless the current dropped at the critical points, just the same as when the small retarding field was employed. This seems surprising, but the slow electrons produced may not diffuse to the plate as readily as do 20 volt electrons, or the drop in current may be the result of a small contact retarding voltage between the plate and grid G_2, or positive ions of an impurity produced by impacts of the second kind with excited helium atoms may diffuse to the plate. If the latter explanation should be the correct one, then both the current drop observed in the Franck method and the rise in current measured in the Lenard method are due to positive ions reaching the plate. At any rate, since the methods employed give results for helium in agreement with spectroscopy, they are thought to be practical and can be used to determine the critical potential of other substances for which no spectroscopic data exist.

Helium as a calibrating gas. These experiments show that the use of helium as a calibrating gas for resonance and ionization potential measurements as used by Hertz[7] is justified, since the corrected experimental value is 19.85 volts for the first resonance as compared with the spectroscopic value of 19.77 volts. This difference may be due to experimental error. Or it might be thought in accordance with the suggestion of Dymond that the maximum efficiency of resonance occurs at a voltage higher than the true critical potential, thus causing the peaks to come at higher voltage in these experiments than the spectroscopic values. However, Sponer[4] pointed out that it is possible, as in the present case, to apply *one* correction to a volt-scale and bring all critical points in agreement with spectroscopy. This means that either all critical points have a maximum of efficiency right near the critical point or that such a maximum is displaced the *same* volt amount for each critical potential. The first alternative seems the easier one to believe.

Furthermore, Hertz[7] has used helium as a calibrating gas to determine the resonance points for the other rare gases. In the case of neon he found the critical points in terms of helium using its spectroscopic values. Later he[8] actually obtained the neon resonance lines by Lyman's spectroscopic methods. The two methods checked. If the helium peaks were displaced a certain amount due to the resonance-maximum appearing a few tenths of a volt higher than the true critical potentials, the calibration would have been incorrect and the two methods could not have checked. It seems, therefore, reasonable to assume that the efficiency of resonance is appreciable a few hundredths volt above the true critical potential.

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[7] Hertz, Zeits. f. Physik **31,** 463 (1925).

[8] Hertz, Zeits. f. Physik **32,** 933 (1925).

The difference between the first and second critical point. Dymond[5] finds by a new differential method that the difference between the first and second critical potential in helium is 1.0 volt and not 0.8 volt, as is obtained from spectroscopy in the visible and also by Franck by his methods of electron impact. This new result is ascribed by Dymond to the fact that the maxima of resonance efficiency for the two types of impact occur at such electron energies so as to cause this larger difference. However, from Table V it is seen that the present experiments agree with the correct spectroscopic value of 0.78 volt.

The difference between single and double impacts. If the possible double transitions are arranged in order of energy required to produce them as in Table IV, it is seen that the difference between the most prominent peak at 40 volts and the first peak near 20 volts is equal to the transition $1S \rightarrow 2P$. The types AA and AB have only been obtained at the highest pressure used (Fig. 2 E, 16), whereas the value 40.96 volts (corrected) has been obtained consistently. Because this experimental value checks numerically with the type CA, it is ascribed to this transition. In order to understand why this transition should be more probable than the others, the relations between probability of impact and energy of impinging electron must be known. Dymond[5] has pointed out that the probability of double impact is the product of the probabilities of the single impacts at the voltage considered. At 40 volts the probability of type C impact may well be larger than of type A or B, and since at 20 volts the probability of type A is larger than of type B the present result would follow. Conversely it may be deduced from these experiments that near 40 volts the probability of impact for type C is greater than for A or B.

In conclusion I wish to thank Professor R. C. Tolman for his interest in this research.

Gates Chemical Laboratory, California Institute of Technology,
Pasadena, California,
December 23, 1925.

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CHARACTERISTICS OF SHIELDED-GRID PLIOTRONS

BY ALBERT W. HULL AND N. H. WILLIAMS

ABSTRACT

The internal "feed-back" from plate to grid of a pliotron is prevented by electrostatically shielding the two from each other. Specially designed tubes, thus shielded, are described. The *capacity* between plate and control grid was found to be only .006$\mu\mu$F in the best models. These tubes may, therefore, be expected to behave as strictly unidirectional devices at all frequencies, which was found to be true. *Plate-resistance* characteristics are given, and it is shown that the internal plate conductance is negligible compared with the conductance of practical circuits. The plate current thus depends on grid voltage only, i.e., in place of the seven parameters of the three element tube there is but one, mutual conductance.

1. INTRODUCTION

THE tubes described in this paper were specially constructed double-grid pliotrons, whose parts were so arranged that the control grid was thoroughly shielded from the electrostatic influence of the plate. They differ from the "screen-grid" tubes described by Schottky[1] only in arrangement of parts, which is such as to minimize electrostatic capacity between plate and control-grid.[2] This difference is unimportant for ordinary low frequency applications, but is essential to high frequency operation, and makes practical many applications that have hitherto been considered impossible. Some of these applications will be described in a separate paper. The purpose of the present paper is to describe the physical and electrical characteristics of the tubes, which are sufficiently unique, it is believed, to be of interest.

2. CONSTRUCTION

The ideal aimed at is to prevent, so far as possible, any lines of force passing from the plate or its connecting wires to the control-grid or its connecting wires. This is accomplished mainly by electrostatic shielding, which is facilitated by appropriate methods of supporting the electrodes. Figs. 1 and 3 show experimental structures that have been found to give satisfactory characteristics.

The shielding consists of two parts: (1) The grid itself is shielded from the plate by an interposed grid, maintained at a constant positive potential, as in the tubes already familiar.[1,3] Sufficient screening for most circuit conditions may be obtained with wire grids, but measurements show that the wires must be so close together as to intercept a considerable fraction of the electrons, thus reducing the mutual conductance. By making the screen grid of thin, wide slats, placed edge on toward the filament,[4] the shielding may be made as nearly perfect as desired, without offering appreciable obstruction to the passage of electrons. (2) The grid-supporting and leading-in wires must be effectively screened from the plate and its associated wires. This may be accomplished by surrounding them by a grounded conductor as shown in Fig. 1, a structure which was suggested and successfully tried by Mr. D. T. Simonds of this laboratory. This method of shielding has the disadvantage of large grid-to-ground capacity. A better method from this standpoint is to support the grid from the top of the tube, taking care that its wires shall nowhere be exposed to those of the plate (Fig. 2). There will still remain a few lines of force, represented in Fig. 2 by dotted lines, from the outside of the plate to the grid leads. Most of these may be intercepted by a grounded

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[1] W. Schottky, Archiv. f. Electrotechnik **8,** 299–328 (1919).

[2] Schottky points out (*l. c.,* p. 320) that the screen-grid tubes which he described are not suitable for high frequency amplification.

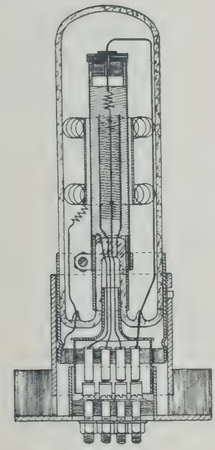

Fig. 1

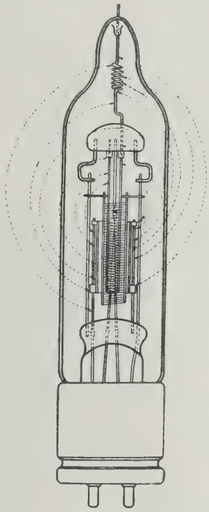

Fig. 2

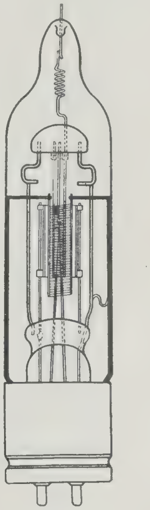

Fig. 3

Fig. 1. Design of "single-end" shielded grid pliotron.

Fig. 2. Design of shielded-grid pliotron with control-grid terminal at top. The shielding is incomplete, as indicated by the dotted lines, which represent lines of force from the plate to the supporting wires of the control grid.

Fig. 3. Design of completely shielded pliotron, with control grid terminal at top. The shielding grid is supported at the top by a metal disc, which is connected to a metal coating on the inside wall of the tube.

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[3] A. W. Hull, Proc. Inst. Rad. Eng. **6,** 5–35 (1918).

[4] Cf Schottky, *l. c.*, p. 318.

metal cylinder fitting closely over the tube. It was found that the few lines which still pass from plate to grid inside the metal cylinder are sufficient to lead to oscillation, unless the screen grid is extended so as to cover the control-grid supports for a considerable distance and the amount of metal in these supports is reduced to a minimum. The simplest and most complete solution found was a metal disc attached to the top of the screen grid (Fig. 3) in conjunction with a metal coating on either the outside or inside wall of the tube. When an inner coating is used it may be connected internally to the screen-grid, as indicated in Fig. 3, or capacity-coupled through the glass wall to an external grounded conductor.

3. Static Electrical Characteristics

These are identical with the characteristics of the double-grid tubes previously described.[1,3] They differ from ordinary three element tubes only in plate resistance, which is infinite or negative at plate voltages lower than that of the screen grid, positive and very high for voltages above the screen grid. Fig. 4 shows a typical plate characteristic, with screen grid at 60 volts. Curve I in the figure represents the current to the plate, curve II the total current to plate and screen grid. The low value and negative slope of the portion *ab* of curve I is due mainly to the loss of secondary electrons from plate to screen grid, whose number increases with plate voltage. The lowness of the portion *cd*, on the other hand, is due only to electrons intercepted by the screen grid. The finite positive slope of *cd*, as compared with the essentially zero slope of the correspond-

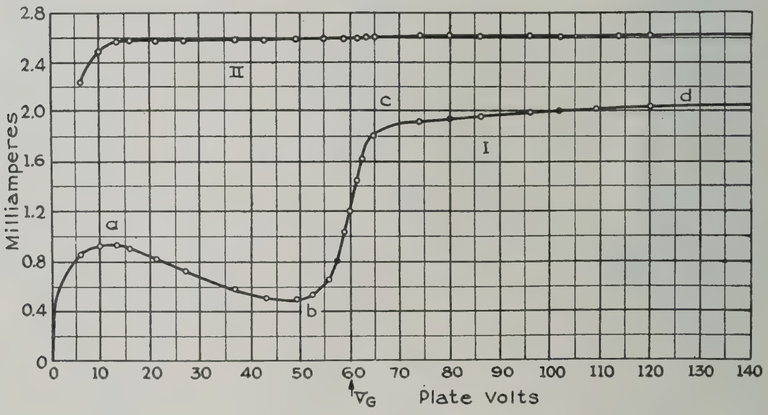

Fig. 4. Plate conductance characteristic of shielded grid pliotron with average secondary emission. The lower curve shows the current to the plate, the upper the total current to plate and screen grid. The potential of the screen grid is indicated by the arrow.

ing portion of the total current curve II, is caused by secondary electrons from the screen grid, only a small fraction of which are able to reach the plate at low plate voltage (70-80 volts in Fig. 4) because of the weak field inside the screen grid, and this fraction increases with plate voltage.

The slopes of both the negative and positive portions of the plate characteristic depend, as is evident from the above description, on the secondary or impact electron emissivity of plate and grid, and the operation of the tubes is greatly influenced thereby. Figs. 5 and 6 show the two extremes of secondary emissivity. The screen grid potential is in both cases 90 volts. Fig. 5 represents a tube whose plate and grid were coated with a thin film of poorly-conducting material, giving high secondary emissivity. The portion of the characteristic below 90 volts has a negative resistance of −11400 ohms, the portion above 90 volts a positive resistance of approximately 100,000 ohms. Fig. 6 is the characteristic of a tube with a nickel-plated plate, the plating current being adjusted to give a fine black deposit. The secondary emissivity is less than 10 percent over the whole voltage range, and consequently the plate resistance both below and above the screen grid potential is positive and very high, viz., 10^6 ohms and 7×10^5 ohms respectively. It is this characteristic to which attention is especially directed in this paper, since the high plate resistance, combined with low plate-grid capacity, makes this tube a very simple circuit element (see section 5).

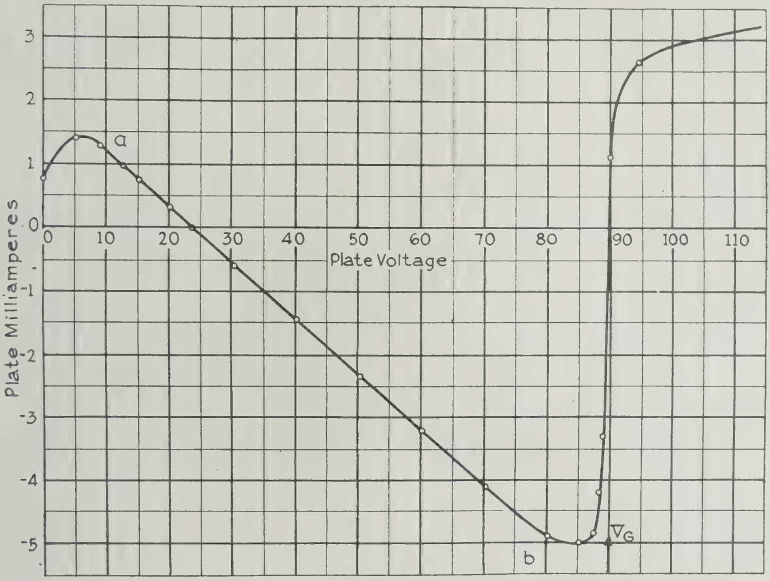

Fig. 5. Plate conductance characteristic of a shielded grid pliotron whose plate has high secondary emissivity.

The mutual conductance characteristic corresponding to Fig. 4, with plate at 90 volts, is shown in Fig. 7. It is about 30 percent lower than that of a three element tube having the same filament and control grid, and a plate at 60 volts in place of the screen grid. This 30 percent loss is due to the electrons intercepted by the screen grid. In other respects this characteristic is exactly similar to the mutual conductance characteristics of three-element tubes. The same is true of the mutual conductance of the other tubes, such as those represented in Figs. 5 and 6, whatever the

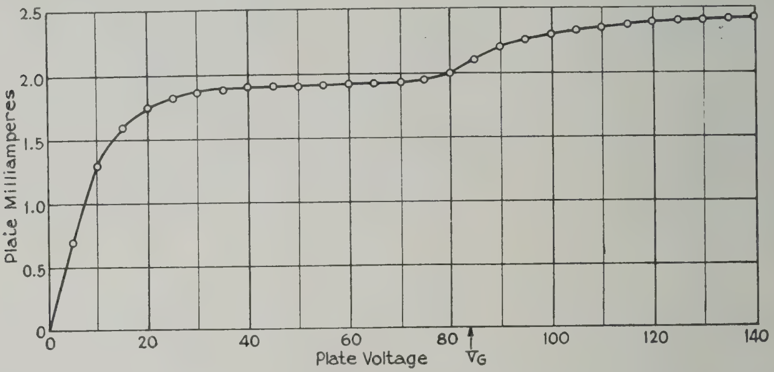

Fig. 6. Plate conductance characteristic of a shielded grid pliotron whose plate has very small secondary emissivity.

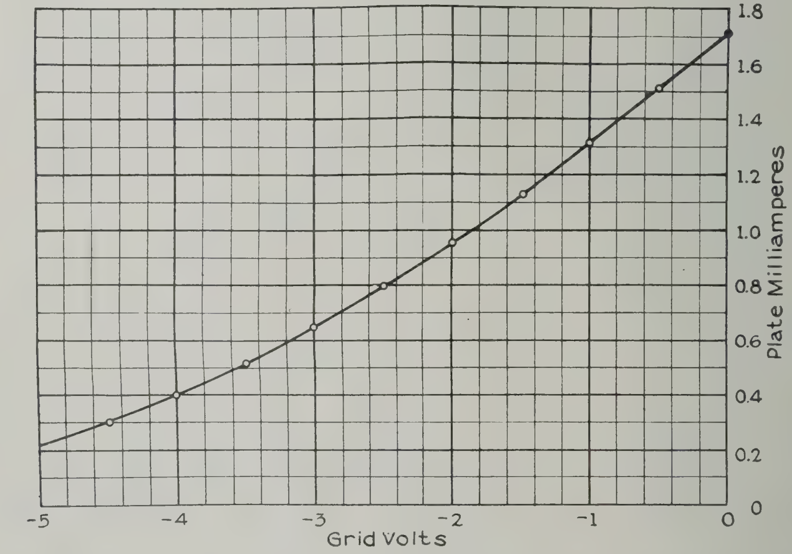

Fig. 7. Mutual conductance characteristic of tube whose plate conductance is shown in Fig. 4, with shielding grid at 60 and plate at 90 volts.

plate voltage. The actual value of mutual conductance is strictly proportional, at any given plate voltage, to the ordinate in the plate resistance curve, Figs. 4, 5, and 6.

4. Internal Capacity

The effective capacity between plate and control grid was measured by feeding a signal to the amplifier through the tube, with cold filament. The signal was impressed upon the plate, and the grid was connected to the input of the amplifier, as shown in Fig. 8. A small variable condenser *c* could be substituted for the tube and adjusted to give the same reading of the detector as was observed when the tube furnished the coupling. Care was required to avoid errors due to wiring capacity. This excluded the use of a parallel plate condenser. The condenser which was found satisfactory consisted of a 5 mil (.125 mm) wire in the axis of a 100 mil (2.5 mm) cylinder, the wire being movable along the axis. End corrections were avoided by leaving the condenser connected to the amplifier and observing the *increase* in length required to produce the same effect as was produced by connecting the plate of the tube. For a typical wire-grid tube this increase was 2.5 mm, corresponding to a capacity of .025 cm, or .0278$\mu\mu$F. The screen grid, in this case, was a helix consisting of 40 turns per inch of 5 mil (.0125 cm) wire. A tube with a slat type of screen-grid, consisting of thin discs of 3 mm width of section placed 3 mm apart, gave a capacity equal to 0.6 mm length of the cylindrical condenser, or .006$\mu\mu$F capacity. The capacity between plate and grid in standard receiving tubes is between 3 and 6$\mu\mu$F without socket, and from 12 to 40$\mu\mu$F with sockets and wiring. The effective plate-grid capacity has thus been reduced to less than 1 percent of the smallest value hitherto used, in the case of the helical wire screen grids, and to 1/5 of 1 percent in the case of the slat grids.

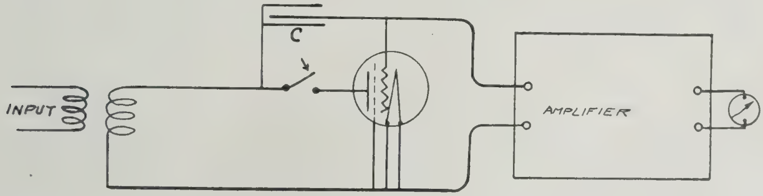

Fig. 8. Circuit used for measuring effective capacity between plate and control grid.

5. The Shielded Tube as a Circuit Element

The circuit behavior of shielded pliotrons is very simple compared with that of ordinary three element tubes. In three element tubes the plate current at high frequency is a complicated function of seven tube constants. These constants are: the variation of plate current with plate voltage (plate conductance) and with grid voltage (mutual conductance), the variation of grid current with plate and grid voltages, and the three internal tube capacities between plate and grid, plate and filament, and grid and filament respectively.

In the case of well shielded tubes these seven tube constants are reduced to one. Two of the four principal tube "parameters," namely, the variation of plate and grid currents with plate voltage, are made zero (as closely as desired), by the shielding. A third, the dependence of grid current upon grid voltage, is zero when the tube is used as an amplifier with proper C battery bias, such that the grid current remains zero.[5] The plate-grid capacity is made effectively zero by the shielding, and all the other tube capacities become merely circuit constants. The shielded grid amplifier tube has, therefore, but a single parameter, *mutual conductance.* The voltage amplification is the product of this mutual conductance by the plate circuit impedance. The amplification that can be obtained per stage is limited only by the impedance that can be built up, by resonance or otherwise; and the number of tubes that can be usefully operated in series is limited only by the terminal conditions, viz., the condition that the input voltage must not be smaller than the "shot effect" or other inherent input disturbance, and that the amplified output cannot be greater than the plate-battery voltage employed for the last tube. The shielded tube is also a strictly unidirectional amplifier, to any degree of strictness that may be desired, as is evident from the capacity tests reported in the last section.

These predictions have been tested and verified by amplification experiments, which are reported in a separate paper.

It will be understood that the purpose of this paper is scientific, and bears no relation to commercial development. Tubes of the type described are not being manufactured, nor is their immediate production contemplated, so far as the authors are aware.

We gratefully acknowledge the cooperation of Mr. Harry C. Thompson in the design and construction of these tubes.

Research Laboratory,
General Electric Company.
December 30, 1925.

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[5] The charging current flowing into the grid because of the grid-to-ground capacity is a circuit and not a tube parameter, since this capacity is simply an additive part of the circuit capacity. This is not true in unshielded tubes, where the effective grid capacity depends upon plate voltage.

MEASUREMENTS OF HIGH FREQUENCY AMPLIFICATION WITH SHIELDED-GRID PLIOTRONS

By Albert W. Hull

Abstract

Tests of cascade high frequency amplification are described, using specially constructed tubes in which the control grid is electrostatically shielded from the plate. These tubes are free from internal feed-back, so that any number may be operated in series. The *voltage amplification* per stage depends only on the circuit impedance, and was found to be 200 at 50 kilocycles, 40 at 1000 k.c., and 7 at 10,000 k.c. *Total amplifications* as high as 2,000,000 in voltage were obtained and measured at 1000 k.c. It is shown that this is the largest amplification that can be usefully employed at any frequency. At 10,000k.c. a total amplification of 10,000 was obtained. Examples are given of other applications, such as the amplification of small photo-electric currents, where shielding is advantageous.

1. Introduction

IT IS commonly believed that any electrical impulse, however small, can be amplified by modern thermionic valves to any desired degree. This belief is completely justified. The only limitation that need be imposed is that the duration of the impulse shall not be shorter than the time of transit of an electron across the tube.

The practical use of such amplification is limited by two considerations: The difficulty of constructing and operating the amplifier may be prohibitive; and the signal may not be worth amplifying, because of the presence of other stronger impulses from which it cannot be separated.

It is the purpose of this paper to show how the first of these limitations, the difficulty of building and operating the amplifier, can be avoided by the use of properly constructed tubes.

The difficulty of building amplifiers is due to instability, caused by "feed-back" of electrical energy from the output circuit to the input circuit. If the impulse thus fed back is in opposite phase to the input signal the amplification will be reduced; if in the same phase it will be increased or "regenerated," and sustained oscillations will result if the amount of energy thus fed back is greater than the losses in the input circuit. Feed-back due to *external* causes, such as electrostatic or magnetic coupling between output and input circuits, or resistance or inductance in common battery and ground wires, can easily be avoided. The most common and obstinate cause is *internal* coupling, that is, coupling due to electrostatic capacity between plate and grid in the same tube. The energy thus fed back through the tube in ordinary receiving tubes is 10,000 times the amount necessary to sustain oscillation in good tuned circuits, at 1000 k.c.

Three practical methods of avoiding oscillation from this internal feed-back have been employed in the past. The first is to use only a single stage of amplification and to so arrange the circuit that the plate voltage is approximately 90° out of phase with the input (grid) voltage. This is the ordinary regenerative method, and is capable of producing from 10 to 100 fold voltage amplification by careful adjustments.

The second method is to use poorly tuned or high resistance circuits, with a small gain per stage. In this way, by keeping the energy fed back per stage smaller than the circuit losses, total amplifications as large as desired may be obtained. This is a practical method, but requires a large number of tubes, since the safe gain per stage is not more than 3 at 1000 k.c., under ordinary circuit conditions, and decreases rapidly with increasing frequency.

The third method is to neutralize the unavoidable feed-back by an intentional feed-back of opposite phase. The two feed-backs must be balanced within about 1 percent at 1000 k.c. with ordinary tubes and good tuned circuits. If such a balance can be found and maintained for each stage there is no limit to the amplification attainable. The difficulty of obtaining exactly opposite phase relations is very great, however, because of the presence of distributed capacity in the tuning coils, and generally limits the total practical voltage amplification obtainable in this way to the order of 100 fold at 1000 k.c., or 1000 fold at 50 k.c.

The method described in this paper is to avoid feed-back entirely by using tubes so constructed that there is no capacity coupling between plate and control grid. It was found that amplification as large as desired could be obtained at any frequency without instability, with a very small number of tubes.

2. Description of Tubes and Circuit

The shielded-grid tubes and their characteristics have been described in a previous paper.[1] For convenience of reference Fig. 3 of that paper, which represents the type of tube used for these measurements, is reproduced here (Fig. 1). As seen from this figure, the shielding of the control-grid from the plate is accomplished internally by means of an extra grid, maintained during operation at a potential which is constant with respect to ground; and, externally by appropriate arrangement of supporting and leading-in wires and the use of grounded conductors.

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[1] A. W. Hull and N. H. Williams, Phys. Rev. **27,** 432 (1926).

In this way it was found possible to reduce the effective capacity between plate and control grid to less than 1 percent of its value in three-element tubes. This capacity is a measure of the plate conductance, which is therefore reduced in the same ratio and becomes negligible in comparison with ordinary load conductances. The behavior of the tubes is thus greatly simplified as compared with three-element tubes. They become strictly unidirectional valves, whose sole parameter, the change of plate current with grid voltage, is independent of all plate-circuit variables.[2]

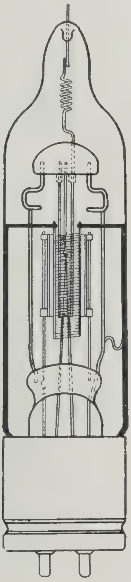

Fig. 1. Drawing of special tube used for high-frequency amplification measurements, showing method of shielding the control grid from the plate.

The circuit used for the cascade amplification tests described below is shown in Fig. 2. It is the ordinary capacity-coupled arrangement, each plate being connected to the 110 volt line through a multiple-tuned circuit LC, and to the next grid through a small condenser c. Resistances r, approximately 1 megohm, maintain the average grid potential at the proper value. The tubes and circuits are mounted in individual boxes covered with tinned sheet iron. These boxes are piled on top of each other, and the top of each tube projects into the box above, making the shielding complete, provided the metal boxes can be maintained at constant potential. Common batteries were used, except as noted below, and the feed to each stage was filtered by a 10 millihenry choke in conjunction with one or more 2 m.f. condensers. It was considered essential that the grounded terminals of all the filter condensers in a single box be soldered to the box at the same point, in order to minimize circulating currents in the box walls. The screen-grids were maintained at 60 volts, unless otherwise stated, and the plates at 110 volts. For convenience in tuning and in measuring amplification, each stage was supplied with a jack, and the method of coupling allowed any tube to be used as detector. In this way the performance of each tube could be checked, and successive stages tuned in, one by one.

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[2] It is assumed that the plate voltage is kept within the operating range.

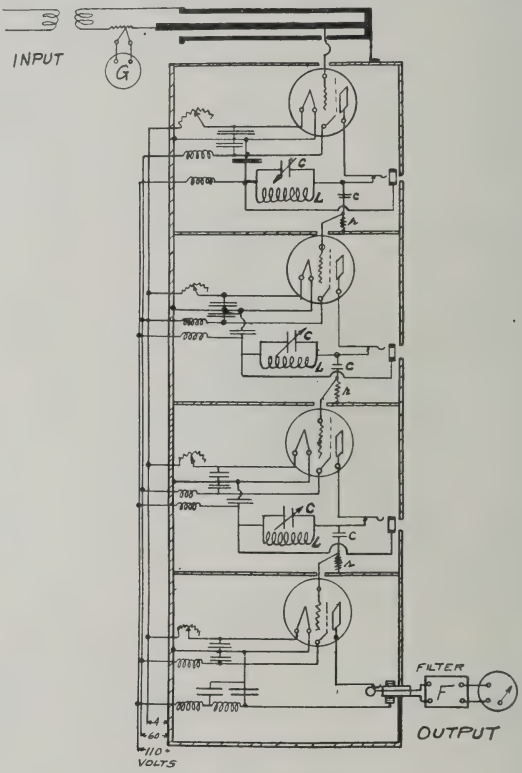

Fig. 2. Diagram of cascade amplifier used for tests at 1000 and 10,000 kilocycles.

The amplification referred to in the following tests is the voltage amplification due to the tubes only, defined as the ratio of r.m.s. alternating voltage of the plate to that of the grid, or of the last plate to that of the first grid in case of more than one tube. Output voltages were obtained in the usual manner by calibration of the detector. The small input voltages required were obtained from the inductive drop in a short section of straight copper rod surrounded by a concentric return conductor, as shown in Fig. 2. For frequencies up to 1000 k.c. this method is reliable and free from difficulties; at 10,000 k.c. care is required in connecting the input system to the amplifier, to avoid capacity-charging currents in the grounding and shielding conductors.

3. Amplification Measurements at Low Radio Frequency (50 k.c.)

Preliminary measurements were made to determine the best type of plate circuit impedance. It was found that no advantage was derived from a step-up transformer of any type. This might have been anticipated, since the high plate resistance of the tube enables it to work efficiently into the highest obtainable impedance. Single tuned circuits were, therefore, used, with condenser feed to the next tube, as shown in Fig. 2. Measurements with coils of different numbers of turns showed, as expected, that the maximum amplification was obtained with the highest possible value of inductance, since this gives the highest impedance.

At low frequencies it is possible to build resonant circuits of very high impedance. Since the voltage amplification is the product of this impedance by the mutual conductance of the tube, high amplifications may be expected. A few measurements at 50 kilocycles showed that a voltage amplification of 200 fold per tube could easily be obtained. The stability and limiting value of multistage amplification was not investigated, but it may safely be assumed from the results at 1000 k.c. that there is no instability at these low frequencies. The measurements of Johnson[3] have shown that there are no tube disturbances at these frequencies except "shot effect," hence the maximum useful amplification is limited only by this ever-present restriction. This limitation is discussed in section 7 below.

4. Medium Frequencies (1000 k.c.)

The circuit shown in Fig. 2 was used. The tubes were first tested singly, and gave voltage amplifications between 40 and 45 at 750 k.c. When operated in series, two tubes gave 1700, and three tubes 75,000, which is equal to the square and cube respectively of the amplification of a single tube, within the limit of accuracy of the measurements. There was no evidence of regeneration. These measurements were made with low impedance input. The set was later used with high impedance tuned input and found to be stable.

A second series of measurements, at 1000 kilocycles, was made with a set containing 6 shielded grid tubes, similar to that shown in Fig. 2. The tubes amplified approximately 40 fold each. Under measuring conditions, i.e., with low impedance input circuit, the first four tubes operated stably in series (the fifth being used as detector) and gave a total voltage amplification of 2 million. This corresponds to 38 fold per stage. All circuits were tuned to exact resonance, and the amplified voltage was found to vary steadily and symmetrically with the tuning of each one of them. The degree of amplification was independent of input voltage from 1 microvolt, the smallest signal that could be distinguished from the "shot effect," to 10 microvolts, which filled the operating range of the last amplifier tube.[4]

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[3] J. B. Johnson, Phys. Rev. **26,** 1 (July, 1925).

The selectivity curve of the four tubes in series (input untuned) is shown in Fig. 3. It coincides very closely with the curve calculated from the circuit constants.[5]

In the first tests with the 4 stage amplification described above it was observed that oscillations resulted when a tuned circuit was substituted for the low-impedance input shown in Fig. 2. The cause of this feedback was found to be external to the amplifier, namely in the common battery supply. The oscillations and all signs of instability disappeared when a separate battery supply was used for the first two stages. The

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[4] It was obviously necessary, in order to avoid saturating the detector, either to use a detecting tube with very low amplification constant, which need not, however, have a shielding grid; or to operate the detector as a tube volt-meter, with variable negative grid bias, adjusted at each reading to give a definite small plate current.

[5] Since mutual inductance is independent of frequency, the theoretical selectivity curve for a single stage is simply the curve of plate impedance, and for n stages the nth power of this impedance. The impedance of a single tuned circuit, viz.

$$z_\omega = \frac{L^2\omega^2+R^2}{\sqrt{(C\omega[L^2\omega^2+R^2]-L\omega)^2+R^2}}$$

reduces, for practical radio circuits, in which R^2 is always negligible compared with $L^2\omega^2$, and for the small values of $\omega-\omega_0$ which are of interest, to

$$Z_\omega = \frac{L^2\omega^2}{\sqrt{4L^2(\omega-\omega_0)^2+R^2}} \qquad (\omega_0 = \text{resonance frequency})$$

The relative impedance is

$$\frac{Z_\omega}{Z_0} = \frac{R}{\sqrt{4L^2(\omega-\omega_0)^2+R^2}} = \frac{R}{\sqrt{157.9L^2(f-f_0)^2+R^2}}$$

where Z_0 is the impedance at the resonant frequency $\omega_0/2\pi = f_0$.

If y is the ordinate of the selective curve, that is, the relative voltage amplification, then for one stage of amplification

$$y = \frac{Z_\omega}{Z_0} = \frac{R}{\sqrt{158L^2(f-f_0)^2+R^2}}$$

and for n stages,

$$y_n = \frac{R^n}{[158L^2(f-f_0)^2+R^2]^{n/2}}$$

same result could undoubtedly have been accomplished with a single common battery supply by better filtering.

Similar results were obtained with 5 stages of amplification. In this case the amplification per stage was reduced, by using coils with smaller inductance, so that the total voltage amplification was still two million, which was the largest that could easily be measured. There was no evidence of instability, with all circuits, including the input, tuned in any desired manner.

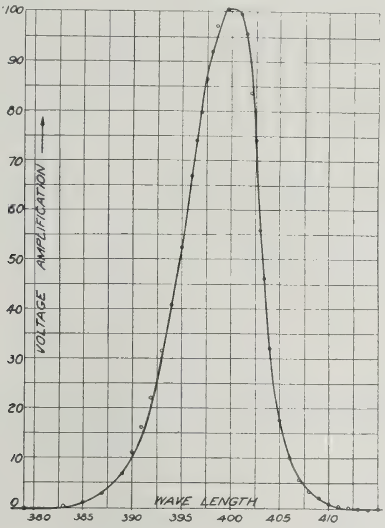

Fig. 3. Selectivity curve of 4 stage amplifier with input untuned, at 1000 k.c. The voltage amplification is 2×10^6.

The observed amplification of 2 million fold in voltage is very near the maximum value that can be usefully employed, because of the presence of shot effect. (This limitation is more fully discussed in section 7.) These tests show, therefore, that any degree of amplification which may be desired can be obtained at 1000 kilocycles, provided external circuit feed-back is avoided.

5. High Frequencies

At high frequencies dielectric and resistance losses are so large that it is not easy to obtain high impedance by resonance, hence the maximum amplification per stage is smaller than at lower frequencies.

Two series of measurements at 10,000 kilocycles (30 meters) were carried out with the 6 tube amplifier described above. In the first series the same condensers (31 plates, 1 mm apart) and same wiring connections, including jacks, were used as in the medium wave-length tests, the coils only being changed. The losses were high, and the impedance at resonance only 8000 ohms (calculated from the ratio of amplification to mutual conductance). This gave a voltage amplification of only 3 per stage. There was no instability, and five stages in series could be operated very simply, with a total amplification of 250.

In the second series of tests, special low loss coils were used, each consisting of 10 turns of 1/4 inch copper tubing, wound in a self-supporting helix of 3 inches diameter and 3 inches total length. The same 31 plate condensers were used (at nearly minimum capacity) but the jacks were by-passed and other insulation losses minimized. The circuit impedance was thus increased to over 16,000 ohms, and the voltage amplification to nearly 7 per stage. It was found that 5 stages in series were still stable, giving a total voltage amplification between 10,000 and 15,000. A series of measurements under these conditions is given in Table I. The variations are due to lack of care in turning, as high accuracy was not sought. The tuning was sharp, but uniform and symmetrical.

TABLE I

5 stage amplification at 10,000 kilocycles
(Circuit like Fig. 2, except jacks. Plate voltage 110, screen voltage 65)

Length of input Inductor 1cm = .00358μh	Current through Inductor	Input volts	Detector reading	Output volts	Voltage amplification
(cm)	(milliamps)		(milliamps)		
0			4.42	0	
3	.37	$.25\times10^{-3}$	4.02	2.5	10000
3	.47	.32	3.85	3.8	12000
3	.82	.55	3.45	7.3	13300
3	1.10	.74	3.30	9.0	12200
3	1.66	1.12	3.05	12.0	10700
9	.32	.64	2.85	16	25000
9	.37	.74	2.95	13.6	18400
9	.42	.84	2.90	14.8	17600
9	.80	1.6	2.80	18	11200
9	.92	1.84	2.65	23	12500
12	.32	.86	2.95	13.6	15800
12	.37	1.00	2.90	14.8	15800
12	.80	2.15	2.85	18	7500

Tuning the input circuit under these conditions caused oscillation. Since these tests were made with the same common battery supply which led to oscillation at 1000 k.c., it is believed that the cause of oscillation in this case was the same, namely insufficient filtering of the power supplied from the common batteries to the individual tubes. The degree of instability was about the same as at 1000 k.c. and could presumably be cured in the same way, by separate battery supply. This has not been tried.

There is every reason to believe that still shorter wave-lengths could be amplified directly in the same manner. The simplest procedure with short waves, however, is to allow them to beat with a local oscillator to give a difference frequency of 10,000 k.c., which can then be amplified as just described. In this way it should be possible to amplify wave-lengths as short as 2 or 3 meters, with no greater delicacy of adjustment than is required to amplify wave-lengths of 400 to 600 meters with the customary intermediate frequency of 50 kilocycles.

6. Discussion of Stability

The conditions under which oscillation can occur from internal capacity feed-back are easily seen from the simplified circuit shown in Fig. 4, which is the a-c. equivalent of Fig. 2. Each plate is capacity coupled to the control grid of the same tube by an effective capacity C_0.[6] Since these capacities are all in series, the nth plate is coupled to the first grid by a capacity C_0/n. This capacity decreases only arithmetically with successive stages, while the amplification increases geometrically. It is evident, therefore, that a stage must eventually be reached, if there were no attenuation, where the energy fed back from the last tube to the first would be greater than the input circuit losses.

The energy thus fed back is attenuated at each stage by the losses of the tuned plate circuit, which includes the capacities to ground of the plate and grid, the grid leak resistance, and the internal plate-resistance of the tube. This is equivalent to a well-known type of filter circuit, whose attenuation may be calculated by the methods described by Campbell and others,[7] provided the terminal impedances are properly adjusted. In the present case a simpler procedure is sufficient. The problem is this: Given a series of identical tubes and circuits, each tuned to approximate resonance, what is the maximum amplification per stage at which self-sustained oscillations are impossible. The only phase relations that need be considered are those favorable to maximum regeneration, since the phases of tuned circuits change so rapidly with tuning that this condition can hardly be avoided, when dealing with more than one stage. This condition is satisfied by exact resonance, which gives the maximum gain per stage, and brings the voltage of each plate in phase with that of the grid of the preceding tube. The plate impedances are then pure resistances, R. Denoting the voltages at successive stages by e_1, e_2, e_3 (Fig. 4) the currents in the various branches are given by the following equations:

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[6] This is called "effective" capacity because it is not a capacity which can be measured in an ordinary capacity bridge. It may be defined as the number of lines of force from the plate that end on the grid per unit potential difference; or as the equivalent ordinary capacity that would have the same alternating-current admittance.

[7] G. H. Campbell, Bell. Sys. Tech. J. **1** (Nov. 1922);
O. J. Zobel, Bell Sys. Tech. J. **2,** 1–47 (Jan. 1923); **3** (Oct., 1924);
L. Cohen, J. Frank Inst. **195,** 641–54 (1923).

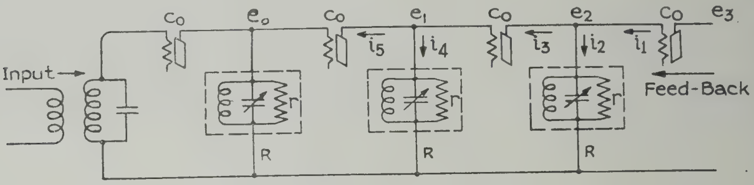

Fig. 4. Simplified diagram of circuit of Fig. 2, showing feed back.

$$i_1=(e_3-e_2)C_0\omega$$
$$i_2=e_2/R$$
$$i_3=(e_2-e_1)C_0\omega$$
$$i_4=e_1/R$$
$$i_5=e_1/\sqrt{R^2+(1/C_0\omega)^2} \qquad \text{(approx.)}$$
$$i_1-i_2-i_3=0$$
$$i_3-i_4-i_5=0$$

For all cases of interest R^2 may be neglected in comparison with $(1/C\omega)^2$. Elimination of e_2 and the five currents between these equations then gives for the relative voltage of the first grid due to feed-back from the third:

$$e_3/e_1=(1/RC_0\omega+2)^2-1 \tag{1}$$

The condition for stability is that this attenuation ratio shall be greater than the two stage amplification. If μ is the amplification per stage, this condition is

$$e_3/e_1=(1/RC_0\omega+2)^2-1>\mu^2$$

or

$$\mu<1/RC_0\omega+2 \tag{2}$$

with sufficient approximation.

The resistance R may be expressed in terms of amplification and the mutual conductance g_m and plate resistance r_p of the tube:

$$\mu=\frac{g_m}{1/R+1/r_p} \tag{3}$$

Substituting this value of R in Eq. 2, one obtains for the maximum stable amplification,

$$\mu<\sqrt{g_m/C_0\omega+(1/2r_pC_0\omega-1)^2}-1/2r_pC_0\omega+1 \tag{4}$$

For screen grid tubes $1/r_p$ is negligible, and Eq. 4 becomes

$$\mu<\sqrt{g_m/C_0\omega+1}+1 \tag{5}$$

In the above tests $g_m=400\times10^{-6}$, $C_0=.028\times10^{-12}$. At 1000 k.c. ($\omega=6.3\times10^6$) Eq. 5 gives $A<49$. The actual amplification per stage was between 40 and 45. Hence the condition was a stable one, but the margin of stability was small. At 10,000 k.c. ($\omega=63\times10^6$) Eq. 5 gives $A<19$. The maximum amplification actually used was 7. To attain an amplification of 19 would require a load impedance of 45,000 ohms, which is probably higher than can be obtained in practical circuits at this frequency. If this is so, the amplifier would be stable at this frequency under all load conditions, provided external sources of feed-back are avoided.

These calculations show that the plate-grid capacity of these tubes, although it has been reduced by shielding to less than 1/100 that of the best three electrode tubes, is barely small enough for stable high frequency amplification. A value 1/4 as great, such as was obtained by the use of a slat type of screen grid,[1] and such as can be obtained with wire grids with a slight sacrifice in mutual conductance, would be ample under all circuit conditions at any frequency.

According to Eq. 4, which is applicable to any kind of tube, the maximum stable amplification with 3 element tubes having a mutual conductance of 400μmhos and plate resistance 30,000 ohms, and with the minimum plate-grid capacity of 2.5$\mu\mu$F, should be 5 at 1000 k.c. Space charge grid tubes, with 4 times the mutual conductance of the single grid tube and the same plate-grid capacity and plate resistance, should be capable of nearly ten fold per stage without instability. The attainment of these values requires special wiring. With ordinary sockets and wiring the total plate-grid capacity is seldom smaller than 12$\mu\mu$F, which reduces the possible stable amplification for three-element tubes at 1000 k.c. to 2.4, and for the space-charge grid tube to less than 5.

With 3-grid tubes,[8] utilizing the advantages of both space-charge and screen grids, the maximum stable voltage amplification per stage at

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[8] Cf W. Schottky, Archiv. f. Electrotechnik **8**, 321 (1919).

1000 k.c. should be over 100, according to Eq. 5, for a tube with plate-grid capacity of .025, and over 200 for .006$\mu\mu$F capacity. At least 3/4 of this higher value, viz., 150, should be capable of realization with practical circuits such as were used in the above tests.

7. Limit of Useful Amplification, Due to Shot Effect

It was observed in the tests at 1000 k.c. that the detector tube showed a small signal even when none was impressed upon the input circuit. This spontaneous generation of oscillations, which is known as "shot effect,"[9] has already been observed and studied under circuit conditions identical with those here used.[10] It is due to shock excitation of the plate circuits—principally that of the first tube, which receives the greatest amplification—by the individual electrons that constitute the plate current. The total r.m.s. voltage thus produced, which is the vector sum of these elementary shock excited voltage oscillations, depends on their total number, that is, on the plate current, on the charge of the electron, on the capacity and power factor of the circuit, and on the degree of space charge. For ordinary radio-frequency tuned circuits, and emissions such as are used in receiving tubes, this r.m.s. voltage lies between 10 and 100 microvolts.

The existence of this shot effect sets a limit to total useful amplification. Amplification ceases to be useful when the shot voltage originating in the first tube fills the detector. For example, if the first tube, in order to amplify 40 fold, must use a plate current so large and circuit damping so small that its shot voltage is 20 microvolts, then with 2 million fold total amplification the amplified shot voltage will be $(2\times10^6/40)\times20\times10^{-6}=1$ r.m.s. volt.[11] This is nearly the maximum amplitude that can be handled by ordinary detecting tubes. It can easily be shown that, for a given degree of selectivity, the ratio of amplified signal to shot noise is independent of circuit conditions, and depends, for a given signal, only on the mutual conductance of the first amplifier tube. The above example was calculated for a mutual conductance of 400μ mhos, which is an average value for receiving tubes. Hence the limit of useful amplification with ordinary tubes may be taken as a million fold in voltage. With a special input tube of high mutual conductance, and a low impedance detector, a maximum of 10,000,000 fold may be utilized. These limits depend upon no fault of tube or circuit, but upon the charge of the electron.

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[9] W. Schottky, Ann. d. Physik, **57**, 541–67 (1918); **68**, 157–76 (1922).

[10] A. W. Hull and N. H. Williams, Phys. Rev. **25**, 147–73 (1925).

[11] The actual value observed in the above tests was 1.3 volts. When a signal is added to this the energies add, so that the observed voltage is the square root of the sum of squares of signal and shot voltage. As an example, a sine voltage of 2 microvolts impressed upon the grid of the first tube gave an amplified voltage reading at the grid of the detector of 4.8 volts. A deflection corresponding to 1.32 volts was observed with no signal, due to the shot effect. The amplified voltage due to the signal of 2 microvolts was, therefore, $\sqrt{(4.8)^2-(1.32)^2}=4.6$ volts. In this case, in order to distinguish the signal from shot effect, it was necessary to use a detector tube with the unusually large range of 4.8 volts.

The above maximum values refer to tube amplification, beginning with the grid of the first tube. Any increase of signal voltage *before* it is impressed upon the amplifier, by transformation or resonance, is added gain.

At frequencies below 10 k.c. there are other disturbances, originating in the tubes and circuits, which are from 10 to 100 times larger than the shot effect.[3] Hence at these low frequencies, namely in the audible and sub-audible range, the maximum useful amplification is between 10,000 and 100,000.

8. OTHER APPLICATIONS

The above description of cascade amplification has been given in full because the results, especially at the higher frequencies, can be obtained practically in no other way. There are other problems, which, though soluble with ordinary tubes, are greatly facilitated by the use of shielded tubes. Two examples will be given.

The first example is the amplification of small rapidly varying currents, such as the photo-electric currents produced by light from successive small areas of a picture, that is to be transmitted by wire or radio. The limit to the speed with which such small aperiodic currents can be reproduced is set by the total effective grid-to-ground capacity, which must be charged or discharged in order to change the grid potential. In the ordinary method of amplifying such currents, the photo current is made to flow through high resistance r (Fig. 5) and the resulting potential difference e at the terminals of r is amplified. The maximum value of r for any given frequency is determined by the capacity of the system, as follows: The photo current i flows through the resistance r and effective grid-to-ground capacity C in multiple, and is given by

$$i=i_r+i_c=e/r+C\,de/dt$$

hence $de/dt+e/Cr=i/C$. Solution of which is:

$$e=ir(1-\epsilon^{-t/Cr}) \qquad (1)$$

e will therefore reach 2/3 of its final value ir in a time given by $t/Cr=1$. (2)

If t is given, the *maximum* allowable value of r is thus determined, viz.

$$r=t/C \tag{3}$$

The capacity C is made up of three parts in multiple, viz., the anode-cathode capacity of the photo cell, the grid-filament capacity of the pliotron, and the effective grid-plate capacity of the pliotron. The latter is μ times the actual grid-plate capacity, where μ is the actual amplification.

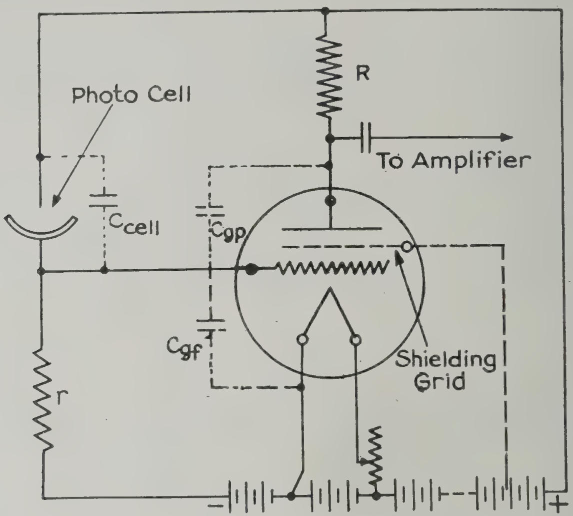

Fig. 5. Circuit for amplifying photoelectric currents, showing advantage of shielding.

Hence $C=C_{cell}+C_{gf}+\mu C_{gp}$

or, taking the three measured capacities as approx. equal

$$C=(\mu+2)C_{Pg} \tag{4}$$

Substituting these values of r and C in Eq. (1) gives for the maximum voltage at the grid

$$e_g=it/(\mu+2)C_{gP} \tag{5}$$

The amplified voltage at the plate is μ times this, viz.,

$$e_p=\mu e_g=\mu it/(\mu+2)C_{gP} \tag{6}$$

It is seen that nothing is gained by amplification, since the fraction $\mu/(\mu+2)$ increases but little with μ. In other words, the photo-electric current i cannot be amplified appreciably by the first amplifier tube, provided it is of the three-element type. This sets a limit to the smallness of the non-sinusoidal current i which can be amplified at any given frequency $1/t$, since the voltage at the *plate* of the first amplifier tube must not be smaller than the shot voltage originating in this tube.

If a shielded-grid amplifier is substituted for the three-element tube, as indicated in Fig. 5, the effective grid-ground capacity is simply its measured capacity, and instead of the fraction $\mu/(\mu+2)$ in Eq. (6) we have approximately $\mu/3$. Since values of μ as high as 100 are easily attainable with shielded tubes at the frequencies under discussion, the amplified voltage e_p will be more than 30 times that obtainable with a three element tube, and the minimum current that can be reproduced will be correspondingly increased.[12]

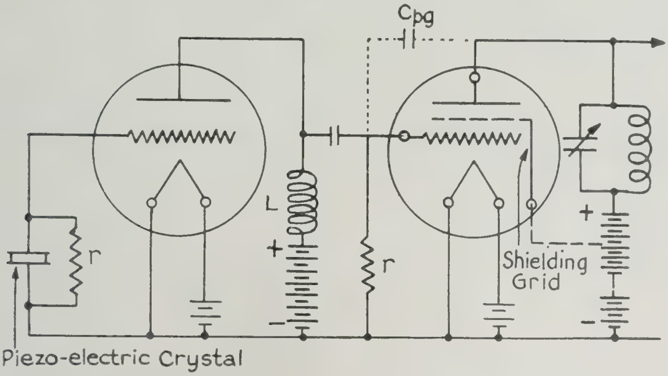

Fig. 6. Crystal-controlled oscillator circuit, showing use of shielded-grid amplifier to prevent change of frequency.

A second example of a useful, but not essential, application of shielded grid tubes is in connection with the utilization of exact standards of frequency for the measurement or control of other frequencies. It is well known[13] that a piezo-electric crystal, such as quartz, may be used to control the frequency of a vacuum tube oscillator, giving extreme constancy. With proper choice of circuit constants and with the crystal maintained at constant temperature, the frequency remains constant to less than 1 part in a million, independent of all ordinary fluctuations of supply voltage, or such changes of circuit constants as are incident to temperature variation or chance mechanical movements.

In order to use such a standard it is necessary to couple it to another system, which will generally react upon the standard and alter its

[12] The gain in minimum reproducible current will not be quite 30 fold, since, if all attempts to amplify with the three element tube are abandoned, the resistance in its plate circuit can be made very low, which will somewhat reduce the shot effect.

[13] W. G. Cady, Phys. Rev. **19**, 1 (1922); Proc. Inst. Radio. Eng. **10**, 83 (1922); **12**, 805 (1924).

frequency. The reaction is smallest when the standard is loosely coupled to the grid of another tube, as shown in Fig. 6. Even in this case, however, tuning the plate circuit of the second tube will in general change the frequency of the standard by 10 to 100 parts in a million, due to the internal capacity reaction between plate and grid of the second tube. This reaction may be balanced by an equal reaction of opposite phase, in the well-known manner, and the effect on the standard circuit thus reduced. But the degree to which this has been accomplished can be ascertained only by comparison with another standard. By using a shielded tube for the second amplifier, as indicated in Fig. 6, all danger of reaction may be avoided, and the frequency made independent of the tuning of the utilization circuit to any desired degree.

It will be understood that the purpose of this paper is scientific, and bears no relation to commercial development. Tubes of the type described are not being manufactured, nor is their immediate production contemplated, so far as the author is aware.

RESEARCH LABORATORY,
GENERAL ELECTRIC CO.,
December 30, 1925.

THE ELECTRIC MOMENT OF CO_2, NH_3, AND SO_2

By C. T. Zahn

Abstract

Dielectric constant of N_2, CO_2, NH_3 and SO_2.— By an improved heterodyne null method previously described, measurements were made of the dielectric constant at atmospheric pressure of the carefully purified gases, over a range from 300° to 400° from just above the liquefaction point. These results as well as all others found by the author are represented by the Debye equation $(\epsilon-1)vT=AT+B$, where ϵ is the dielectric constant, T the absolute temperature, and v the specific volume. The values found for A are .000958 (CO_2), .000768 (NH_3), and .001433 (SO_2); and for B are .003 (CO_2), 1.740 (NH_3), and 2.167 (SO_2). The anomaly observed by Jona and attributed to association was not observed except possibly to a slight degree in NH_3. The values of the *electric moment of the molecules* calculated from the constant B differ from Jona's values by 7 percent. It is believed that the explanation of the difference is to be based on the fact that the anomaly is not due to association but to surface effects on the metallic plates of the condenser. The values obtained for the electric moment are, in c.g.s., e.s. units$\times 10^{18}$, .06 (CO_2), 1.44 (NH_3), and 1.611 (SO_2). The small value for CO_2 differs from zero by an amount which is less than the experimental error.

IN an article by Jona[1] on the variation of the dielectric constant of gases with temperature marked deviations from the Debye straight line were recorded in the cases of water vapor, methyl alcohol, and sulfur dioxide near the liquefaction point. These deviations were attributed to association with an accompanying increase in the electric moment of the molecule. In a series of measurements[2] on the halogen hydrides no such deviations from the Debye theory were observed even though the measurements were made near the liquefaction points of the gases studied. For this reason it was thought worth while to make a further investigation of this anomalous effect. To this end measurements were made on several of the gases studied by Jona.

The experimental method used has been described by the author in the above mentioned paper[2] on the electric moments of the halogen hydrides. A heterodyne null method is used in which the beats between the oscillations from two separate electron-tube generators operating at frequencies of about 1,000,000 and 1,001,000 cycles per second are adjusted to the frequency of an electrically driven tuning fork, the small change of capacity due to the introduction of the gas into the measuring condenser being compensated by a large change in a large capacity in series with this condenser.

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[1] M. Jona, Phys. Zeits. **20**, 14 (1919).

[2] C. T. Zahn, Phys. Rev. **24**, 400 (1924).

According to Debye's theory[3] the dielectric constant of a gas is given by the equation

$$(\epsilon-1)vT=AT+B$$

when ϵ is the dielectric constant, T is the absolute temperature, and v is the specific volume referred to the volume occupied by 1 cc of an ideal gas at 0°C and 760 mm Hg. For an ideal gas $v=T/273$ but for vapours this is corrected by the use of van der Waals' equation. A is a constant which represents the electric polarization due to induced distortion in the molecule and B is a constant which represents the orientation polarization and is proportional to the square of the electric moment of the molecule.

$$(\mu^2=1.198\times 10^{-36}B)$$

If $(\epsilon-1)vT$ is plotted against T there is obtained a straight line of slope A and intercept B which determines μ. For gases of symmetrical structure, i.e., zero electric moment, $B=0$ and the straight line should pass through the origin of coordinates.

Measurements were first made on N_2 as a rough check on the behaviour of the apparatus. Since N_2 is not a polar molecule one should expect zero electric moment for the molecule and the Debye straight line should correspondingly pass through the origin of coordinates. This was found to be the case within the limits of experimental error. It should be noted here that for the measurements on nitrogen the temperature control of the apparatus was not so good as for the other measurements which were made later when an oil bath of large heat capacity was used for the high temperatures. The later measurements are undoubtedly more accurate than those on nitrogen. In the case of nitrogen the maximum deviation from the mean value of $(\epsilon-1)v$ is less than one percent which was the upper limit estimated for the error introduced by the original calibration of the condensers used.[2]

Measurements were also made on CO_2, NH_3, and SO_2. The CO_2 and SO_2 were taken from commercial cylinders and dried and then distilled repeatedly by freezing in liquid air and evaporating, discarding each time small quantities of the gas coming off first and last. NH_3 was obtained by heating concentrated ammonia water and was purified as above.

The measurements are given in Table I and the values of $(\epsilon-1)vT$ are plotted against T in Fig. 1. All these measurements were made by measuring the difference in the capacities of the experimental condenser corresponding to atmospheric pressure and a small pressure of about

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[3] P. Debye, Phys. Zeits. **13,** 97 (1912).

6 cm of the gas under investigation. (This procedure was adopted because it was found that when the condenser was completely evacuated the heat insulation between the plates was good enough to prevent sufficiently rapid equalization of temperature of the two plates.) The results are reduced to atmospheric pressure by assuming that $(\epsilon-1)$ may be regarded as proportional to the pressure for this small correction. In each case, measurements were made to temperatures within a few degrees of the liquefaction points corresponding to atmospheric pressure. These later points are indicated in the figure by vertical broken lines.

TABLE I

Dielectric constant data

T°K	$(\epsilon-1)\times10^6$	$(\epsilon-1)v\times10^6$	$(\epsilon-1)vT$
		Nitrogen	
84.1	1898	572	.0481
197.8	792	572	.1132
273.0	581	581	.1586
562.1	283	583	.3276
		Carbon Dioxide	
199.2	1353	978	.1948
200.6	1345	978	.1962
286.6	926	968	.2774
295.0	909	976	.2878
469.0	561	962	.4512
		Ammonia	
241.7	9280	8142	1.966
274.4	7132	7143	1.962
296.7	6117	6620	1.965
371.4	4018	5452	2.024
456.9	2734	4567	2.086
		Sulfur Dioxide	
265.5	10015	9627	2.547
267.6	9918	9530	2.550
295.5	8176	8770	2.592
297.2	8120	8768	2.606
366.9	5477	7323	2.687
443.8	3911	6336	2.812

The data of particular interest are those for SO_2 and NH_3. For SO_2 Jona obtained at 300°F about a 10% increase of $(\epsilon-1)vT$ over the value corresponding to the limiting slope at higher temperatures; whereas the observations here recorded show no such anomaly, even though the measurements are carried about 35° below Jona's lowest temperature. For NH_3 Jona recorded at room temperature a slight anomaly, whereas Fig. 1 shows no definite deviation for temperatures as low as room temperature, but near the liquefaction point there seems to be a definite increase of about 2%. The obvious inference is that there is some effect that is present only slightly in the present measurements but which was quite appreciable in Jona's work. It is difficult to imagine how such an effect could be attributed to association which should reach a definite equilibrium concentration, unless the time required for association should be comparable to the time between observations. This latter supposition seems very unlikely. In fact it is difficult to see how any effect which is characteristic of the gas itself; i.e., any volume effect could account for the difference in the two sets of observations, whereas the existence of surface layers on the metallic plates might reasonably be responsible for the inconsistencies. Such layers might depend upon the nature of the metal of the condenser and also upon the degree to which the surfaces had been cleaned by baking and evacuation. For example it is possible that a surface which had not been properly cleaned might have entirely different properties as regards adsorption of layers of the gas. In fact some recent experiments of the author on water vapour suggest that there is a surface effect in such measurements.[4]

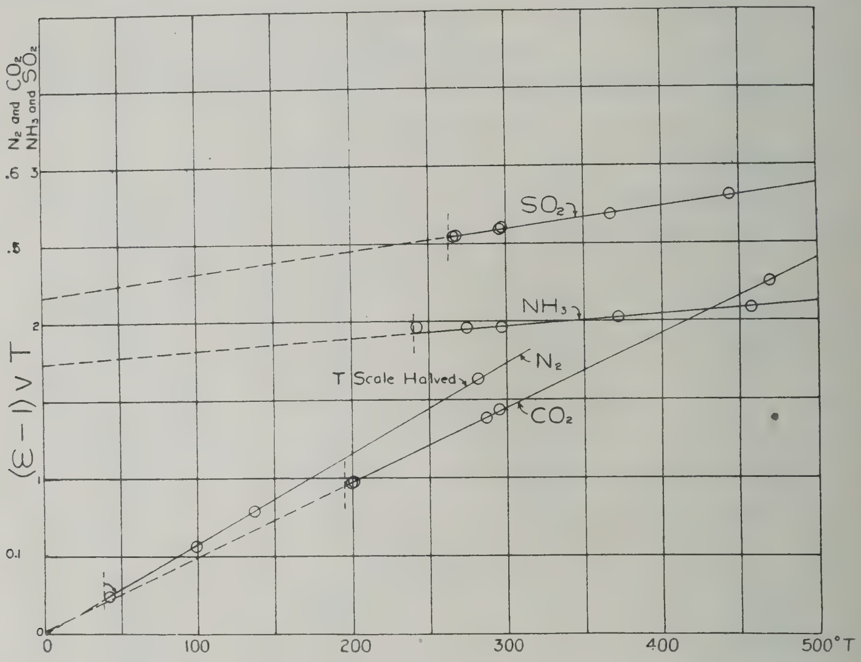

Fig. 1. Variation of $(\epsilon-1)\nu T$ with temperature.

In Table II are given the Debye constants as taken from the data of Fig. 1 together with the values of electric moment given by Jona, for the purpose of comparison. From the figure it would appear that CO_2 has a slight electric moment but considerably less than that given by Jona. In fact the value is so small as to be within the limit of experimental error, and it cannot be stated definitely that CO_2 has an appreciable electric moment. The difference between Jona's values of μ and those taken from Fig. 1 may be due to an error introduced by his equation which was developed on the assumption of the existence of associated molecules. This error would present itself in the reduction to standard pressure and would depend on the actual pressures used in the experiments. Since he has not given these pressures, no definite comparison can be made. The difference in the μ values of Table II is about 7% for NH_3 and SO_2 and is well beyond the limit of experimental error for both observers.

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[4] C. T. Zahn, Phys. Rev. **27**, 329 (March, 1926).

TABLE II

The Debye constants

Gas	$A \times 10^6$	B	$\mu \times 10^{18}$ (c.g.s.,e.s. units)	$\mu \times 10^{18}$(Jona)
CO_2	958	.003	.06	.303
NH_3	768	1.740	1.44	1.53
SO_2	1433	2.167	1.611	1.76

In Table III is given a resumê of all the observations taken of the variation of dielectric constant with temperatures with the apparatus described previously by the author.[2] There are here included the measurements on the halogen hydrides, those here described, and measurements taken on four hydrocarbons in collaboration with Dr. Charles P. Smyth.[5]

TABLE III

Resumê of dielectric constant data

Gas	$A \times 10^6$	B	$\mu \times 10^{18}$ (c.g.s.,e.s. units)
HCl	1040	.895	1.03
HBr	1212	.52	.79
HI	1856	.12	.38
C_2H_2	1334	0	0
C_2H_4	1444	0	0
C_2H_6	1501	0	0
a-C_4H_8	2694	.115	.37
N_2	580	0	0
CO_2	958	.003	.06
NH_3	768	1.74	1.44
SO_2	1433	2.167	1.61

In conclusion the author wishes to acknowledge his indebtedness to Professor K. T. Compton for helpful advice and to Mr. E. W. Cheney for assistance in making some of the measurements.

NATIONAL RESEARCH FELLOWSHIP.
PRINCETON UNIVERSITY.
November, 1925.

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[5] C. P. Smyth and C. T. Zahn, Jour. Amer. Chem. Soc. **47,** 2501 (1925).

APRIL, 1926 PHYSICAL REVIEW VOLUME 27

FORCES ON A RIGID MAGNETIZED CONDUCTOR

By E. H. Kennard and S. C. Wang

Abstract

The *forces on magnetized material carrying current* are examined from the standpoint of the electron theory. The true distribution of forces depends upon the minute structure of the material and so is at present unknown in the general case; it is even doubtful whether the partial force on the current alone is $\mathbf{j}\times\mathbf{B}$. For a *rigid body* two sets of forces equivalent to the unknown actual ones are obtained: the first set consists of a force per unit volume equal to $\nabla_H(\mathbf{I}\cdot\mathbf{H})+\mathbf{j}\times\mathbf{B}$ together with an additional torque per unit volume $\mathbf{I}\times\mathbf{H}$; the second consists simply of a force per unit volume equal to $m\mathbf{H}+\mathbf{j}\times\mathbf{H}$, ($\mathbf{H}=$ magnetic intensity, $\mathbf{B}=$induction, $\mathbf{j}=$current density, $\mathbf{I}=$intensity of magnetization, $m=$free pole density). The first set may resemble the actual forces somewhat more closely than the second, but the second set is so much simpler that it is recommended for general adoption. If a set of stresses is preferred to body forces, the set commonly used is recommended, which consists of a tension along the tubes and a pressure perpendicular to them, each equal to $\mu H^2/8\pi$, with no assumption whatever as to the stresses in rigid bodies where μ does not have a constant value: this set corresponds to neither of the laws of force.

The *rotating-magnet experiment* recently repeated by Zeleny and Page is discussed and the torque is ascribed by preference to forces on the free poles.

A PROBLEM in electromagnetics that is still unsettled is that of the forces that act upon a permanently magnetized conductor carrying a current. The source of difficulty here lies in the fact that permanent magnetism occurs only in solids, and in the case of a solid body only the total force and torque upon it are accessible to experiment and not the detailed distribution of force throughout the body. The question is further complicated by the attempt one naturally makes to separate the force into two parts, a force upon the current, and a force upon the magnetic material. Since these two partial forces cannot possibly be separated in observation, such a separation can be effected only upon the basis of theoretical assumptions of some sort.

In such a situation the theorist often tries first a simple extension to the new case of laws that are well established for simpler cases. In the present case, however, such an attempt meets with serious difficulty. For one thing, the force upon a current can be observed separately only in media where magnetic intensity and induction are equal; when we pass to magnetic material, we are in doubt which of these vectors, or what combination of them, should be taken to determine the partial force upon the current. In the second place, the field in a current-containing region differs notably from that due to magnets in that it possesses no scalar potential. The forces exerted by such a field upon a small plane current are not the same as the forces upon the "equivalent" magnetic dipole, as is easily seen in certain simple cases. What, then, shall we assume to be the action of such a field upon a piece of magnetized matter placed in the field? No experimental answer to this question is possible, for the simple reason that such fields can only be realized in the presence of distributed currents and the force is then masked by the unknown partial force upon the current.

Under these circumstances a definite answer seems to be possible only on the basis of a constitutive theory of magnetism and current. Today the safest basis appears to be the electron theory, and it is the purpose of the present paper to treat the problem systematically from this point of view; no adequate treatment on this basis seems to occur in the literature. All that we shall need to borrow from the electron theory is the assumption that magnetic fields and electromagnetic forces are due to moving electricity acting according to the laws of Lorentz; for simplicity we shall speak in terms of electrons, but our discussion will have nothing to do with the attempts, hitherto largely unsuccessful, to account for the specific magnetic or electric properties of particular kinds of matter. The results of the investigation are carefully summarized in the Abstract above.

The problem is made particularly timely by the recent interesting repetition by Zeleny and Page[1] of the experiment in which a bar magnet is set into rotation about its magnetic axis by allowing a current to enter it in the middle and leave at one end. The mode in which the torque to be expected is calculated by these authors, although simple, does not seem to us to be, as it stands, free from logical objection. Our principal purpose here is not to criticize this calculation, but we think it may assist in clarifying the subject if we first explain our objections to it.

The rotating magnet as treated by Zeleny and Page. In treating the theory of the rotating magnet, the authors imagine the current to enter in the form of a symmetrical "sheet" AB; and they suppose that either the magnetization or the distribution of current in the sheet is symmetrical about the axis. They then calculate the torque in two steps. The torque "exerted by the magnet upon the current" is calculated from the assumption that this force is proportional to the induction; the basis of this assumption is presumably the electron theory. The "torque exerted by the current on the magnet" is then calculated from the forces on the free poles, and a novel procedure is here introduced. Taking first the simple case in which the current enters in a thin sheet AB, it is pointed out that there is a distribution of free poles *CC* on the material just above the sheet which is equal and opposite to that on the end of the magnet at *B*, and obviously the torques on these two sets of poles will exactly cancel each other; the net torque on the magnetic material is therefore concluded to be zero. The *total* torque as thus calculated was found to agree with the experimental value.

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[1] Zeleny and Page, Phys. Rev. **24,** 544 (1924).

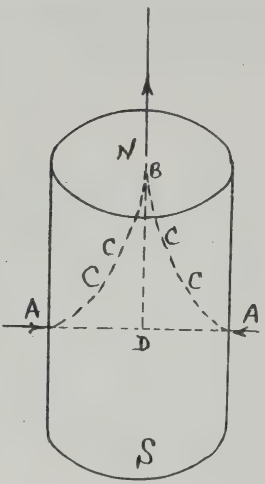

Fig. 1.

An important point would seem, however, to have been overlooked. Presumably the current is supposed to flow through a thin but finite slice of the material; this slice will then have poles, and the torque on the upper poles of the slice will clearly be just equal and opposite to the torque on the contiguous poles *CC* just above the current. If account is taken of this torque on the slice the total torque on the magnetic material no longer vanishes. Probably the writers of the article knowingly rejected the torque on the slice as negligible, on the excellent and generally valid principle that forces on indefinitely small things must likewise be indefinitely small. But the present case is peculiar in that the current density in the slice is very high and some of the derivatives of the magnetic field, upon which the torque must depend, are very large; if the slice is made indefinitely thin these quantities become indefinitely large (at least relatively). For this reason it appears to the present writers that an additional argument is necessary at this point.

Apparently the difficulty can be met only by invoking some new law of force for application to the current-carrying slice. Perhaps with an emendation of this sort the calculation would appeal to some as satisfactory. In the opinion of the present writers, however, the simultaneous use of two different laws of force in dealing with a single piece of matter seems complicated and confusing and likely to lead to errors. This objection seems to gain in weight when we turn to the actual case in which no part of the magnet is entirely free from current.

In the experiments referred to, the magnet was also replaced by a brass cylinder and it was observed experimentally that this cylinder experienced the same torque for a given current as did the magnet provided the magnetic flux was the same in the two cases; this result was taken to support the view that the "poles of a symmetrical magnet contribute nothing to the torque" under the circumstances of these experiments. It seems obvious, however, that such a conclusion can be drawn only after we have shown that the partial torque on the current is the same in the two cases, in spite of the difference that in one case the flux is due entirely to field-strength whereas in the other case it is largely flux of magnetization; and since this cannot be shown experimentally, we are thrown back upon theory again, so that the results with the brass cylinder hardly seem to throw much light upon the problem.

The true nature of these difficulties as we see them will become clearer after our general discussion of the law of force, to which we now turn.

FORCES AND TORQUES ON A RIGID MAGNETIC BODY TRAVERSED BY CURRENTS

Nomenclature used:

$\mathbf{B}$ = the magnetic induction.

$\mathbf{H}$ = the magnetic intensity.

$\mathbf{H}'$ = the partial magnetic intensity at a point in the magnetic material obtained by omitting the magnetic field of the entire body.

$\mathbf{I}$ = the magnetic moment per unit volume or the intensity of magnetization.

$m = -\operatorname{div} \mathbf{I}$ = the free pole density.

$\mathbf{j}$ = the current density.

First form of the law of force. We shall begin our calculation with the simple assumption that the electron streams constituting the current go through the material in straight paths on the molecular scale. In such a case, since the average value of the true magnetic intensity along these paths is, according to the electron theory, the magnetic induction $\mathbf{B}$, the average force on the moving electricity per unit volume is evidently $\mathbf{j} \times \mathbf{B}$.

In calculating the force on the molecular circuits of the magnetic body, we shall make use of the following general principle: The work done by electromagnetic forces on the molecular circuits of a piece of rigid magnetic matter, when the latter is virtually displaced in any manner, is $\int \delta_{H'}(\mathbf{I} \cdot \mathbf{H}')d\tau$ integrated over the piece of the material, where $(\mathbf{I} \cdot \mathbf{H}')$ denotes the scalar product of the two vectors, $\delta_{H'}(\mathbf{I} \cdot \mathbf{H}')$ is the change of $(\mathbf{I} \cdot \mathbf{H}')$ at a point of the material after the displacement and the subscript H' indicates that the intensity of magnetization $\mathbf{I}$ is to be fixed in magnitude and direction relative to the material in calculating the change.

According to this principle the x, y, and z components of the force due to $\mathbf{H}'$ on the molecular circuits of the material per unit volume are

$\mathbf{I}\cdot\partial\mathbf{H}'/\partial x$, $\mathbf{I}\cdot\partial\mathbf{H}'/\partial y$ and $\mathbf{I}\cdot\partial\mathbf{H}'/\partial z$ respectively; or the vector force $\mathbf{f}'$ per unit volume is $\nabla_{H'}(\mathbf{I}\cdot\mathbf{H}')$, where the subscript H' denotes again that the differentiation is to be made on $\mathbf{H}'$ alone.

Adding to $\mathbf{f}'$ the force on moving electricity, $\mathbf{j}\times\mathbf{B}$, we get for the total translational force per unit volume on the material due to $\mathbf{H}'$

$$\mathbf{F}'=\nabla_{H'}(\mathbf{I}\cdot\mathbf{H}')+\mathbf{j}\times\mathbf{B}\ . \tag{1a}$$

It will be shown later that in the above equation $\mathbf{H}'$ can be replaced by $\mathbf{H}$ without affecting the value of the total force on the rigid body. Hence we can also employ instead of $\mathbf{F}'$ a force $\mathbf{F}_1$ per unit volume given by[1]

$$\mathbf{F}_1=\nabla_{H}(\mathbf{I}\cdot\mathbf{H})+\mathbf{j}\times\mathbf{B}\ . \tag{1}$$

The field will also exert a torque on the magnetic matter tending to rotate the molecular circuits about an axis perpendicular to the plane of the vectors $\mathbf{I}$ and $\mathbf{H}'$. If θ is the angle between $\mathbf{I}$ and $\mathbf{H}'$ the magnitude of this torque will be $\partial/\partial\theta(\mathbf{I}\cdot\mathbf{H}')=-IH'\sin\theta$, so that the torque per unit volume exerted independently of the translational force $\mathbf{F}'$ will be

$$\mathbf{T}'=\mathbf{I}\times\mathbf{H}'\ ; \tag{2a}$$

or, replacing $\mathbf{H}'$ by $\mathbf{H}$ for the reason just stated, we can employ as the independent torque per unit volume

$$\mathbf{T}=\mathbf{I}\times\mathbf{H}\ . \tag{2}$$

The total vector torque on the body about the origin will thus be

$$\mathbf{L}=\int[\mathbf{r}\times\mathbf{F}_1+\mathbf{I}\times\mathbf{H}]\,d\tau=\int\{\mathbf{r}\times[\nabla_H(\mathbf{I}\cdot\mathbf{H})+\mathbf{j}\times\mathbf{B}]+\mathbf{I}\times\mathbf{H}\}\,d\tau\ , \tag{3}$$

where $\mathbf{r}$ is the radius vector from the origin to the element $d\tau$.

We shall now drop the assumption that the conduction electrons go through the material in straight paths on the molecular scale. Since the reaction of the force on the body, as exerted on the rest of the system, will depend only upon dimensions or properties of that body on the physical scale, it is evident that the total force on the rigid body will remain the same as long as the paths of the electrons of two similar systems do not differ on the physical scale. Hence Eqs. (1a) to (3) will certainly lead to correct results for an actual rigid body.

We cannot, however, attach with certainty any definite physical meaning to the two terms of Eq. (1) or (1a) separately. To say that the one is the force on the current and the other that on the magnet would be justified only if the paths of the electrons were known to be straight lines on the molecular scale or if we could ascertain by some other means that the average force on moving electricity really is $\mathbf{j}\times\mathbf{B}$ per unit volume.

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[1] This force is the same as that given in Livens' Theory of Electricity, p. 589, but the torque (2a) is not there given. If Curl $H=0$, $\nabla_H(I\cdot H)=(I\cdot\nabla)H$ and Eq. (1) and (2) agree with the forces on p. 270 of Livens' book.

These equations cannot even be regarded as giving the true total force-action per unit volume upon the material, for there will probably be additional forces and torques which arise from local attractions and repulsions between the molecular circuits and the moving electrons and which are not included in the force-action as calculated from such mean values as the ordinary current density and magnetization. The probability of such effects is easily seen by considering special cases. This local action will not affect the motion of the body as a whole, of course, but it may alter the distribution of the forces and so may give rise to strains; for this reason, as is well known, magnetostrictive effects cannot be calculated from equations such as (1) to (3).

Second form of the law of force. From Eq. (1a) the x-component of the total force on the body is

$$P_x=\int\left[\mathbf{I}\cdot\frac{\partial\mathbf{H}'}{\partial x}+(\mathbf{j}\times\mathbf{B})_x\right]d\tau \tag{4}$$

$$=\int\left[I_x\frac{\partial H'_x}{\partial x}+I_y\left(\frac{\partial H'_y}{\partial x}-\frac{\partial H'_x}{\partial y}\right)+I_y\frac{\partial H'_x}{\partial y}-I_z\left(\frac{\partial H'_x}{\partial z}-\frac{\partial H'_z}{\partial x}\right)\right.$$
$$\left.+I_z\frac{\partial H'_x}{\partial z}+(\mathbf{j}\times\mathbf{B})_x\right]d\tau$$

$$=\int\left[(\mathbf{I}\times\operatorname{Curl}\mathbf{H}')_x+\frac{\partial}{\partial x}(I_xH'_x)+\frac{\partial}{\partial y}(I_yH'_x)+\frac{\partial}{\partial z}(I_zH'_x)\right.$$
$$\left.-H'_x\frac{\partial I_x}{\partial x}-H'_x\frac{\partial I_y}{\partial x}-H'_x\frac{\partial I_z}{\partial z}+(\mathbf{j}\times\mathbf{B})_x\right]d\tau$$

$$=\int[(\mathbf{I}\times\operatorname{Curl}\mathbf{H}')_x+\operatorname{div}(H'_x\mathbf{I})-H'_x\operatorname{div}\mathbf{I}+(\mathbf{j}\times\mathbf{B})_x]d\tau\,.$$

Substituting Curl $\mathbf{H}'=4\pi\mathbf{j}$, $\mathbf{B}-4\pi\mathbf{I}=\mathbf{H}$ and $-\operatorname{div}\mathbf{I}=m$, we have

$$P_x=\int[(\mathbf{j}\times\mathbf{H})_x+mH'_x+\operatorname{div}(H'_x\mathbf{I})]d\tau\,. \tag{5}$$

By the divergence theorem $\int\operatorname{div}(H'_x\mathbf{I})d\tau$ integrated over the body is equal to $\int H'_xI_ndS$ integrated over a surface immediately surrounding the body. But this surface integral vanishes because **I** vanishes on the surface. Eq. (5) then becomes

$$P_x = \int [mH'_x + (\mathbf{j}\times\mathbf{H})_x]d\tau\ ; \tag{6}$$

and similar results are obtained for P_y and P_z.

Turning now to the total torque, we have from Eqs. (1a) and (2a) for its z-component

$$L_z = \int \left\{ x\left[\mathbf{I}\cdot\frac{\partial\mathbf{H}'}{\partial y} + (\mathbf{j}\times\mathbf{B})_y\right] - y\left[\mathbf{I}\cdot\frac{\partial\mathbf{H}'}{\partial x} + (\mathbf{j}\times\mathbf{B})_x\right] + (\mathbf{I}\times\mathbf{H}')_z\right\} d\tau \tag{7}$$

Here we can operate on the terms inside the two brackets exactly in the same manner as we did in passing from Eq. (4) to Eq. (5). Corresponding to Eq. (5), Eq. (7) becomes

$$\begin{aligned} L_z &= \int \Big\{ x[(\mathbf{j}\times\mathbf{H})_y + mH_y' + \operatorname{div}(H_y'\mathbf{I})] - y[(\mathbf{j}\times\mathbf{H})_x + mH_x' \\ &\qquad + \operatorname{div}(H_x'\mathbf{I})] + (\mathbf{I}\times\mathbf{H}')_z \Big\} d\tau \\ &= \int \Big\{ x[(\mathbf{j}\times\mathbf{H})_y + mH_y'] - y[(\mathbf{j}\times\mathbf{H})_x + mH_x'] + \operatorname{div}(xH'_y\mathbf{I}) \\ &\qquad - H_y'I_x - \operatorname{div}(yH_x'\mathbf{I}) + H_x'I_y + (\mathbf{I}\times\mathbf{H}')_z \Big\} d\tau . \end{aligned}$$

By the divergence theorem the volume integrals of the two divergence terms are equal to two surface integrals which vanish. Hence we have

$$L_z = \int \left\{ x[(\mathbf{j}\times\mathbf{H})_y + mH'_y] - y[(\mathbf{j}\times\mathbf{H})_x + mH'_x] \right\} d\tau\ , \tag{8}$$

with similar expressions for L_x and L_y.

According to Eqs. (6) and (8) the resultant force and torque are the same as if the body experienced a force per unit volume equal to $m\mathbf{H}' + \mathbf{j}\times\mathbf{H}$. To this force we can, however, add a force $m(\mathbf{H}-\mathbf{H}')$ without affecting the total force and torque, for the forces thereby added are simply the forces on the free poles of the body due to their own fields. Hence the total force and torque on the body are the same as if the only force acting were a force per unit volume given by

$$\mathbf{F}_2 = m\mathbf{H} + \mathbf{j}\times\mathbf{H}\ . \tag{9}$$

It is evident that if we replace $\mathbf{H}'$ by $\mathbf{H}$ in Eqs. (6) and (8) and trace back step by step, we will finally get Eq. (1) instead of (1a) and (2) instead of (2a), as already stated in connection with these equations.

Discussion of the two forms of the law. We now have two simple laws of force between which we can choose. The first form of the law[2] is represented by Eqs. (1) and (2); in this form there is a force $\mathbf{j}\times\mathbf{B}$ on the current, and then there are a force $\nabla_H(\mathbf{I}\cdot\mathbf{H})$ and a torque $\mathbf{I}\times\mathbf{H}$ which together represent a tendency of the magnetic material to move so as to increase the flux of magnetic intensity in the direction of the magnetization. This form of the law has an advantage in that it almost certainly resembles the true distribution of forces more closely than does the other distribution given by Eq. (9), without, however, any strong claim to be correct in detail; it has been pointed out before that in reality neither the separate terms of $\mathbf{F}_1$ nor $\mathbf{F}_1$ as a whole can be regarded as representing with certainty the true distribution of forces upon the material. This form has also the advantage of accounting directly for effects not only upon rigid bodies but upon incompressible liquids as well (one has only to deduce from this law the body forces represented, for instance, by the middle term of Eq. (407) in Jeans' Electricity and Magnetism, 4th ed.).

On the other hand, the second form of the law of force as given in Eq. (9) has the great merit of simplicity.[3] It involves only a force, without the addition of a torque, and the expression for the force is especially simple, since both parts of it involve the same field vector; the force consists of a force $m\mathbf{H}$ upon the free poles, which are so useful in calculating magnetic fields, and a force $\mathbf{j}\times\mathbf{H}$ upon the current. Furthermore, in case of need the second form can be easily made to give a distribution of forces exactly like that given by the first form by applying it, not to the free poles of the whole body, but to the poles of the elements; the first term in the force equation then gives $\nabla_H(\mathbf{I}\cdot\mathbf{H})-\mathbf{I}\times\text{Curl}\,\mathbf{H}$ and thus compensates for the difference between $\mathbf{j}\times\mathbf{H}$ and $\mathbf{j}\times\mathbf{B}$. Such a procedure seems very natural in the case of a liquid, whose elements are capable of relative motion; thus this case also can be handled without difficulty by means of the second form of the law, and the calculation is found to be little longer than if the first form is employed.

After weighing these considerations carefully, the present authors would recommend the retention or adoption in elementary treatises of the second law of force, Eq. (9), as the basic form. In advanced treatises both laws may, of course, be given.

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[2] The law is given in this form in Livens' Theory of Electricity, pp. 270, 589.

[3] This form is equivalent to the law stated by A. Einstein and J. Laub (Annalen der Phys. **26**, p. 541, 1908, Eqs. (7) and (8)); the only difference is that they represent the first part of the force as acting upon the poles of the elements instead of the free poles.

In any case, it would seem to be best not to mix the two laws in treating the same rigid body. For instance, in the paper of Zeleny and Page previously referred to, the force $m\mathbf{H}$ on the poles as required by the second law is combined with the force on the current in the form $\mathbf{j}\times\mathbf{B}$ as required by the first law; this undesirable combination was, in our opinion, the source of the difficulties discussed above.

To avoid misunderstanding, a word should be said about the force on a wire surrounded by a magnetic fluid, which equals $\mathbf{j}\times\mathbf{B}_0$, where $\mathbf{B}_0$ is the value that $\mathbf{B}$ would have at a point on the wire if a short section of it and if its current were removed. Neither of the laws deduced above gives a force of this magnitude as acting upon the wire (consider, for instance, the case in which the wire itself is non-magnetic). The deficiency is made up by a purely mechanical differential pressure of the fluid upon the wire; the existence of such a pressure would become evident if the wire were surrounded by a narrow empty space and a sheath carrying no current, for this part of the force would then act upon the sheath. Thus the fact that the total force on the wire is $\mathbf{j}\times\mathbf{B}_0$ does not lend support, as might be thought, to what we have called the first form of the law.

In conclusion we shall compare briefly the treatment, in terms of the two laws, of the case referred to above in which a current enters a cylindrical bar magnet along a circle AA (see Fig. 1) round its middle and leaves at one end along the axis of rotation. The calculation can be put into a very simple form if we first note that the torque is necessarily independent of the path taken by the current through the magnet, because the difference in distribution between any two paths consists of a distribution of current confined to the interior and surface of the magnet, and interaction between such a distribution and the magnet cannot produce a net torque on the magnet itself. We can therefore suppose the current to enter symmetrically around the ring AA, flow radially to the center, and then follow the axis to the end.

If we now use the first law of force, we see at once from symmetry that the torque in Eq. (2) and the first term in Eq. (1) contribute nothing to the torque. A simple calculation then shows that the second term of (1), $\mathbf{j}\times\mathbf{B}$, gives a torque equal to iN, where i = total current, N = flux of induction across the section AA of the magnet.

If we use, instead, the second law, represented by Eq. (9), we find by a simple calculation that the second term, $\mathbf{j}\times\mathbf{H}$, gives a torque iN_H where N_H = flux of intensity H through the section AA; this torque is small if the magnet is very slender. The first term is then easily seen to yield a torque on the poles equal to $i(\Sigma m)/4\pi = iN_1$, where N_1 flux of magnetization through AA. Since $N_H+N_1=N$, the total torque is iN.

It is clear that in this special case the first law of force leads more simply to the final result. It appears, however, to the present writers that this case is a peculiar and atypical one, and that in spite of the disadvantage in this case the second form of the law is nevertheless the best one to choose whenever it is desired to state a single universal law applicable to all cases.

The peculiar symmetry of this case also enables us to go a little further than usual in regard to the true location of the forces: if both the magnetization and the current are symmetrically distributed around the axis, then it seems clear that local forces can have no component perpendicular to a plane through the axis so that the torque-producing component of force at each point must really be the corresponding component of $\mathbf{j}\times\mathbf{B}$; but the same statement cannot be made of other components of the force, nor can it be asserted with confidence that $\mathbf{j}\times\mathbf{B}$ represents the force acting directly upon the current.

Stress-equivalents for the law of force. The set of forces given by Eq. (9) is identical with that of Eq. (20) on page 282 of the third edition of Maxwell's Electricity and Magnetism. It is shown there that this set of forces is equivalent to the following set of stresses:

(a) a tension along the lines of force equal to $H^2/8\pi$,

(b) a pressure in all directions at right angles to the lines of force numerically equal also to $H^2/8\pi$.

Many other sets of stresses can be assigned which will account correctly for the force action upon a rigid body, for this depends only upon the stresses over its surface. The choice of a set will be dictated purely by convenience, since the occurrence of local action precludes any attempt to calculate the strains of magnetostriction in the general case. In practice, the stresses are commonly taken to be of the magnitude $\mu H^2/8\pi$ at points where there is a constant scalar permeability; this expression has the well-known advantage of accounting correctly for the behavior not only of rigid bodies but also of incompressible isotropic liquids. The most practical plan would seem to be to continue this practice and simply to assume nothing in regard to the stresses in material where such a permeability does not exist, for the latter happens only in rigid bodies where the magnitude of the stresses is immaterial anyhow.

It is interesting to note that the body forces due to the stresses of magnitude $\mu H^2/8\pi$ correspond to neither of the two laws of force developed above.

Cornell University,
Nov. 17, 1925.

NOTE ON "FORCES ON A RIGID MAGNETIZED CONDUCTOR"

By John Zeleny and Leigh Page

Abstract

In reply to the criticism by Kennard and Wang of our theory of the torque on a cylindrical magnet through which a current is passing, it is pointed out that there is a rational distinction between the torque exerted by the current on the magnet and that exerted by the magnet on the current passing through it. From the point of view of Ampere's theory of magnetism, the first torque is zero and the second is $iN/2\pi$, in electromagnetic units, both for the case of a symmetrical current sheet and asymmetrical magnetization and for the case of symmetrical magnetization and an asymmetrical current. Therefore on the modern conception that magnetic properties are due to electric currents and not to magnetic charges *per se*, the torque on a cylindrical magnet carrying a current cannot correctly be ascribed to the action of the current on the magnet in either of the two cases under discussion, contrary to the contention of Kennard and Wang.

IN a recent paper[1] we deduced a new formula for the torque on a cylindrical magnet through which a current is passing in terms of the flux N and the current i and we verified this formula experimentally over a considerable range. In the paper preceding this note Kennard and Wang criticize our theory on the grounds (a) that it is impossible to make any rational distinction between the torque exerted by the current on the magnet and that exerted by the magnet on the current passing through it, (b) that the point of view adopted by us in calculating the first torque is inconsistent with that used in calculating the second and that we obtained the right result only by a procedure of dubious legitimacy, (c) that it is preferable to ascribe the torque to forces on the free poles rather than to forces on the current passing through the magnet.

At the start we wish to make clear that our point of view is that of Ampère's theory of magnetism, that is, that the magnetic properties of a magnet are due to intra-molecular or intra-atomic currents of constant intensity and not to magnetic charges *per se*. The question as to whether these currents are due to revolution of electrons about a nucleus or not is irrelevant to the analysis of the phenomenon. To be sure, we found it convenient at one point of our argument to substitute for the Amperian circuits a fictitious density of magnetism in accord with the usual procedure. This device, however, did not involve a change in point of view.

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[1] Zeleny and Page, Phys. Rev. **24,** 544 (1924).

In answer to objection (a) we observe that the field H due to the current in the magnet as well as that outside is a perfectly definite quantity which is calculable in the same manner whether the current passes through an iron magnet or a brass cylinder. Its value depends only on the value i of the steady current and the geometrical configuration of the circuit. By the torque exerted by the current on the magnet we mean the torque exerted by this field on the magnet. Similarly the field due to the Amperian circuits responsible for the magnetic properties of the iron is a perfectly well defined quantity. The average value of this field, as is well known, is the magnetic induction B. By the torque exerted by the magnet on the current passing through it we mean the torque exerted by this field on the current. So we maintain that on the Amperian theory of magnetism (which we believe is generally accepted by physicists) there is a rational distinction between the two torques calculated in our paper.

Objections (b) and (c) are answered by a consideration of the calculation of the two torques defined above. The force on a current element is given by the force equation of the Maxwell-Lorentz theory. Substituting B for the magnetic intensity in this equation, the torque $iN/2\pi$ exerted by the magnet on the current is obtained, as given in our original paper. To be sure, since B is the average value of the field inside the magnet, the natural assumption is made that the electrons carrying the current do not show any preference for the weaker or stronger portion of the field in their passage through the material. *The agreement of our experimental results with the theory, certainly in the case of a symmetrical current sheet, is an a posteriori justification of this assumption.* Moreover, we fail to see that Kennard and Wang's analysis of the problem avoids this assumption. In calculating the torque exerted by the current on the magnet we made use of a fictitious density of pole, and showed that, for the two cases considered, there is no torque due to the action of the current on the magnet. Kennard and Wang seem to consider that this substitution of a fictitious density of magnetism for the Amperian molecular currents actually present involves a change in point of view and they make a point of the possibility of the current's passing between the two surfaces of such a fictitious magnetic shell. Now it is well known that the field of a current circuit is equivalent to that of a magnetic shell, whose periphery coincides with the circuit, only at points outside the shell. Therefore when considering the interaction of the current and the magnet the fictitious magnetic shells introduced must be so placed that the current under consideration is never located in the interior of a shell. This is always possible since the only condition determining the form and location of the shell which has to be satisfied is that its periphery shall coincide with the circuit. However, it is a simple matter to show that the torque exerted by the current on the magnet vanishes without introducing a fictitious magnetic charge. The proof is given below; the two cases considered in the original paper being treated separately.

Case I. The distribution of current in the sheet is symmetrical. In this case the lines of force of the field due to the current are circles in planes perpendicular to the axis of the magnet with centers on this axis. As the force on any current element at a point P in the magnet is perpendicular to the field at this point it lies in the plane determined by the axis and the point P. Hence it has no moment about the axis of the magnet. Therefore there is no torque exerted by the field of the current on the Amperian circuits in the magnet, no matter how asymmetric the magnetization of the magnet may be.

Case II. The magnet is symmetrically magnetized. Take an annular ring of radius p and cross section ds about the axis of the magnet. Use cylindrical coordinates p, ϕ, z, the last named being measured parallel to the axis of the magnet. Let J_p, J_ϕ, J_z be the sums of the components of all the current elements of the Amperian circuits per unit volume in the directions of increasing p, ϕ, z respectively, *the current elements of the current i being excluded from these sums.* Denote by H_p, H_ϕ, H_z the components of the field due to i resolved in these same directions and by dF_p, dF_ϕ, dF_z the components of the force exerted by H on the current elements comprised in J which are contained in the volume element $pd\phi ds$. Then the only component of dF which has a moment about the axis is dF_ϕ. Now

$$dF_\phi = (-J_pH_z + J_zH_p)\,pd\phi ds$$

But in a symmetrically magnetized bar $J_p = J_z = 0$. Therefore the force F_ϕ vanishes, whatever H_z and H_p may be, that is, whatever form the current circuit i may have. It should be noted that symmetrical magnetization does not mean that $J_\phi = 0$ throughout the magnet, and it is only because J_ϕ does not enter the expression for dF_ϕ that we can conclude that dF_ϕ is zero. For instance, if the magnet is magnetized uniformly as well as symmetrically (intensity of magnetization constant and everywhere parallel to the axis) J_ϕ is zero in the interior of the magnet but not at the cylindrical surface. In this case the resultant effect is that of a solenoid wound around the magnet. Incidentally it may be recalled that in our experiments symmetry of magnetization was tested by approaching a second magnet to the suspended magnet and noting whether or not a deflection was produced.

The only possible torques which have been neglected are (a) a torque on the magnet due to the field of the magnet, (b) a torque on the current due to the field of the current. Obviously there can be no torque (a). As regards (b) the treatment of case I above shows that there can be no torque of this character when the distribution of current in the sheet is symmetrical. When the distribution of current is not symmetrical the torque (b) on the portion of the current in the rotating system may not vanish and cases can be imagined in which it might be of appreciable magnitude, but it is obviously quite negligible in the usual set up such as was employed in the experiments described in our original paper.

Finally, the rational distinction which we have made between torque on the current and torque on the magnet vindicates our claim that the experiments with a brass cylinder placed in a magnetic field prove experimentally that the resultant torque is on the current and not on the magnet.

Sloane Physics Laboratory,
Yale University,
December 3, 1925.

APRIL, 1926 PHYSICAL REVIEW VOLUME 27

HALL EFFECT IN EVAPORATED FILMS OF IRON, COBALT, NICKEL, PALLADIUM, AND PLATINUM

By H. B. Peacock

Abstract

Hall coefficients of evaporated films.—The Hall coefficients for films of Fe, Co, Ni, Pd, and Pt, 6 to 270$\mu\mu$ thick, deposited on surfaces at a distance less than the mean free path from the evaporating filament, were measured. For films of the ferromagnetic metals, Fe, Co, Ni, the Hall coefficients were respectively 1.4, 4.9, and 7.8 times the values for the corresponding metals in bulk, these factors being in the order of the atomic numbers of the elements. For the paramagnetic, negative Hall effect metals, Pd and Pt, the Hall coefficients were 0.66 and 0.64 times the values for the metals in bulk. The increased Hall effect for the films of the ferromagnetic metals seems closely related to ferromagnetism, although Ni, the least ferromagnetic of the three, shows the greatest variation. Films of Ir and Rh, formed at a distance less than the mean free path from the evaporating filament, showed for Ir a positive Hall effect as in bulk, and for Rh no detectable effect.

Specific resistance of evaporated films.—The ratios of the specific resistances of the evaporated films to the specific resistances of the corresponding metals in bulk were found to be 3.1 (Fe), 23.0 (Co), 25.0 (Ni), 4.4 (Pd), 14.0 (Pt), 10.8 (Ir), 12.0 (Rh).

Saturation of the Hall e.m.f.—Curves show that the saturation of the Hall e.m.f. occurs for evaporated Fe at a slightly lower magnetic induction than for Fe in bulk; for Co, at about 12,500 gauss as compared with 13,500 for bulk; and for Ni, at about 2500-3000 as compared with 6000 for bulk. It is significant that the magnitudes of these variations from bulk values, like the corresponding variations in the Hall coefficient, occur in the order of these elements in the periodic table.

Effects of Heating.—Heating films of the ferromagnetic metals during or after deposition decreased the Hall coefficients and specific resistances to approximately the values for the metals in bulk. It also caused a shift in the value of the magnetic induction necessary to produce saturation of the Hall e.m.f. toward that for the metals in bulk. No effect of heating was observed in the paramagnetic metals.

Interpretation.—Evaporated films may differ from bulk metal in the size of the crystalline grains, in the nature of the material between them or in an asymmetry of the crystalline grains which may be an important factor in the causes of the Hall effect.

Introduction

STEINBERG[1] has shown that for evaporated films of the diamagnetic, negative Hall effect metals, silver and copper, the Hall coefficients were smaller than for the same metals in bulk, while for iron, which shows a positive Hall effect, this coefficient was considerably larger than the bulk value. Also, for evaporated films of iron, the magnetic induction necessary to produce saturation of the Hall e.m.f. was about half as large as is required for bulk iron. For all of these metals, the Hall coefficients were found to be independent of the thickness. He found the specific resistance of these films to be much larger than for the massive metals, which is in agreement with the work of Weber and Oosterhuis,[2] and also observed the usual critical thickness. He believed the Hall effect to be practically independent of the structure except as it affects the magnetic condition of the crystals. The work of Sorenson[3] shows that the magnetic properties of evaporated ferromagnetic films are different from massive metals but no suggestion is offered as to the cause underlying the results observed by Steinberg on iron.

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[1] J. C. Steinberg, Phys. Rev. **21**, 22 (1923).

The present study repeats Steinberg's work on iron and extends the investigation to some other metals of the same group in the periodic table. This group of metals was chosen because it contains both paramagnetic and ferromagnetic elements as well as metals having positive and negative Hall coefficients. It is, therefore, possible to test whether the variations in the Hall effect in evaporated iron are due to its ferromagnetism or to the fact that its Hall effect is positive. If it is due to the latter, cobalt and iridium might be expected to have similar variations; if due to ferromagnetism, nickel, in spite of its negative Hall effect, and cobalt, might be expected to give results similar to iron.

On account of the difficulty of obtaining the metals in the proper form for evaporation, only iron, cobalt, nickel, palladium, platinum, iridium and rhodium were investigated. Of these, the last three and especially the last two were so difficult to evaporate[4,5,6,7] that only a few films were studied. The effect of heat treatment during and after deposition was investigated in some of the films. Films of nickel and cobalt were examined microscopically for crystal structure.

EXPERIMENTAL

The method of producing the evaporated films was the same as that used by Steinberg[1] with a few improvements in apparatus. Two microscope slides, one above and the other below the filament, were used for the deposition and by means of a heating element beneath the lower

[2] Weber and Oosterhuis, K. Akad. Amsterdam, Proc., **19,** 597 (1917).

[3] A. J. Sorensen, Phys. Rev. **24,** 658 (1924).

[4] J. H. I. Roberts, Phil. Mag. **25,** 271 (1913).

[5] W. Crookes, Roy. Soc. Proc., **A86,** 461 (1911).

[6] Harker and Kaye, Roy. Soc., Proc. **A88,** 522 (1913).

[7] Kaye and Ewen, Roy. Soc., Proc., **A89,** 58 (1913–14).

plate, a temperature difference could be maintained between the two allowing deposition of two films under differing temperature conditions. The approximate temperatures were measured by means of very fine copper-constantin thermocouples held in close contact with the plates.

The pressure in the tube during evaporation was in most cases 0.00075 mm of mercury or less as indicated by a McLeod gauge. In the later experiments, a mercury vapor trap was inserted between the pumps and the tube to eliminate the mercury vapor from the tube. At the pressure used, all parts of the plates were well within the mean free path of the gas in the tube.

The Hall effect, specific resistance and thickness were measured in the same manner and with the same apparatus as was used by Steinberg.[1] In measuring the Hall e.m.f. by the potentiometer method, the average of a number of readings was taken with the field in both directions.

The metals used were the purest that could be obtained in the proper form. Samples of the iron wire of Steinberg[1] and of Sorenson[3] were both used. One piece of nickel wire was obtained from Driver-Harris Company 98.5 percent pure. Another sample was the same as used by Sorensen. In neither the iron nor the nickel was any difference detected in the different samples. The cobalt films were made from cobalt deposited electrolytically on coils of tungsten wire to a depth of 0.25 mm. The differences in melting points and depth of layer probably kept the deposit tungsten-free. The palladium was furnished by Eimer and Amend as "pure." The platinum was Baker and Company's "special commercially pure" and was said to contain 99.5 percent of platinum. Flat strips of iridium and rhodium were produced by grinding down with carborundum wires about 0.7 mm in diameter obtained from the N. E. L. A. Research Laboratory.

RESULTS

Hall effect and specific resistance. The values of the Hall coefficients and specific resistances for the evaporated films are shown in Table I in comparison with the values for bulk metals given by other observers. The Hall coefficient, R, is calculated from equation $R = E\epsilon/\beta I$ in which E is the Hall e.m.f., ϵ the thickness of the film, I the current in the film, and β the magnetic induction at right angles to the plane of the film and to the current. The specific resistance is designated by ρ and the subscripts, e and b, refer to evaporated and bulk metals, respectively. The values of R_e and ρ_e are the mean values for the number of films indicated deposited on places kept as cool as possible and at temperatures approximately the same. The thickness of the films ranged from 13 to

134$\mu\mu$ for iron, 11 to 166$\mu\mu$ for cobalt, 6 to 270$\mu\mu$ for nickel, 10 to 204$\mu\mu$ for palladium and 6 to 36$\mu\mu$ for platinum. Averaging R_e is justified since it is known to be a constant for all thicknesses for a given metal. In determining ρ_e, only those films were included which were thicker than the critical thickness. The values of R_b differ greatly for different observers and there is some question as to what values to use. Smith's[8] values for the first five metals were chosen because his paper also gives other data used.

TABLE I

The Hall coefficients and specific resistances for evaporated films and for bulk metals.

	Evaporated		Metals			Bulk	Metals		
Metal	No. of films	$R_e \times 10^3$(e.m.u.) Value	Mean dev.	$\rho_e \times 10^6$(ohms) Value	Mean dev.	$R_b \times 10^3$ (e.m.u.)	$\rho_b \times 10^6$ (ohms)[10]	$\frac{R_e}{R_b}$	$\frac{\rho_e}{\rho_b}$
26Fe	14	+16	3	35	13	+11.0[8]	10	1.4	3.1
27Co	12	+29	5	216	63	+ 5.88[8]	9.7	4.9	23.0
28Ni	22	−99	13	200	58	−12.7[8]	7.8	7.8	25.0
46Pd	16	− 0.57	0.07	49	14	− 0.86[8]	11	0.66	4.4
78Pt	8	− 0.13	0.03	140	50	− 0.202[8]	10	0.64	14.0
77Ir	2	+ 0.034	0.002	66	5	+ 0.402[9]	6.1	....	10.8
45Rh	2	No effect	......	57	3	No data	4.69	....	12.0

*Since iridium and rhodium films were not deposited within the mean free path, these results must not be considered as conclusive.

The Hall coefficients of the evaporated paramagnetic metals are smaller than in bulk as was found by Steinberg[1] for the diamagnetic metals, silver and copper; while for the ferromagnetic metals, these coefficients are larger than in bulk as was found by Steinberg for iron. It must be concluded that the increased Hall effect in evaporated films is a characteristic of ferromagnetism rather than of the sign of the Hall effect. These variations from bulk, being in opposite directions for different metals, practically eliminate the possibility that the observed results are due to an error in assuming the density of the films to be the same as in bulk.

Effects of heating. Heating films of iron, cobalt and nickel to a temperature of about 300°C during evaporation had the effect of reducing both R_e and ρ_e nearly to the values for the massive metals. For two films deposited at the same time and under the same conditions except for a temperature difference of about 100°C, both R_e and ρ_e were from 25 to 60 percent smaller for the heated film. The effect of heating after deposition was also investigated in nickel films with approximately the same results.

[8] A. W. Smith, Phys. Rev. **30,** 1 (1910).

[9] H. Zahn, Ann. d. Physik **16,** 148 (1905).

[10] Smithsonian Tables.

No effect of heating was observed in the non-ferromagnetic metals.

Saturation effects. It is known that with the ferromagnetic metals the equation $R = E\epsilon/\beta I$ fails to hold for the larger values of β and the Hall e.m.f. is said to become saturated. Steinberg[1] has shown that for evaporated iron this saturation occurs at a much lower value of β than for bulk iron. This result is confirmed only in a general way. Fig. 1 shows $E\epsilon/I$ plotted as a function of β for iron. Curves A, B, C and D, are for evaporated films and the other curve for bulk iron is taken from Smith's[8] paper. These curves show saturations at an induction only slightly less than for bulk metal. Similar curves for cobalt are given in Fig. 2 showing saturation at about 12,500 gauss as compared with 13,500 for bulk. Figs. 3 and 4 show corresponding curves for nickel. For the evaporated films, saturation occurs at about 2500 to 3000 and for bulk at about 6000.

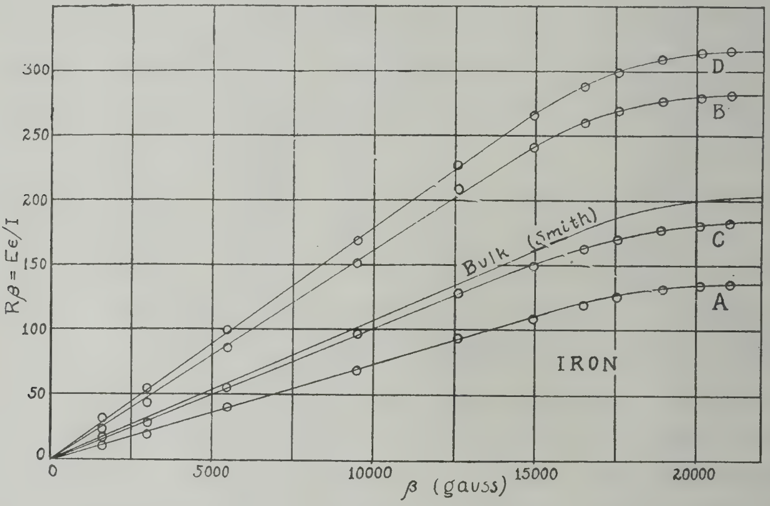

Fig. 1. Saturation of Hall e.m.f. and effect of heat treatment in evaporated iron. A and C are for films heated at a higher temperature.

These curves also show effects of heat treatment of the films which are evidenced in two ways. In the first place, the slopes of the curves give the values of the Hall coefficients, which have been shown to be larger for the less heated films. In Fig. 1, curves A and C are for iron films deposited on heated surfaces, B and D, on surfaces kept as cool as possible. Films A and B were deposited at the same time. Similar curves for cobalt are given in Fig. 2. Curves A and B are for films made at the same time, A being slightly more heated. C is for a film deposited on an especially hot surface, the definite temperature of which is not known. In the curves of Fig. 3 the pairs A,B and C,D are for nickel films made at the same time, respectively, *A* and *C* being deposited at the higher temperatures. Fig. 4 shows effects of heating nickel films after deposition.

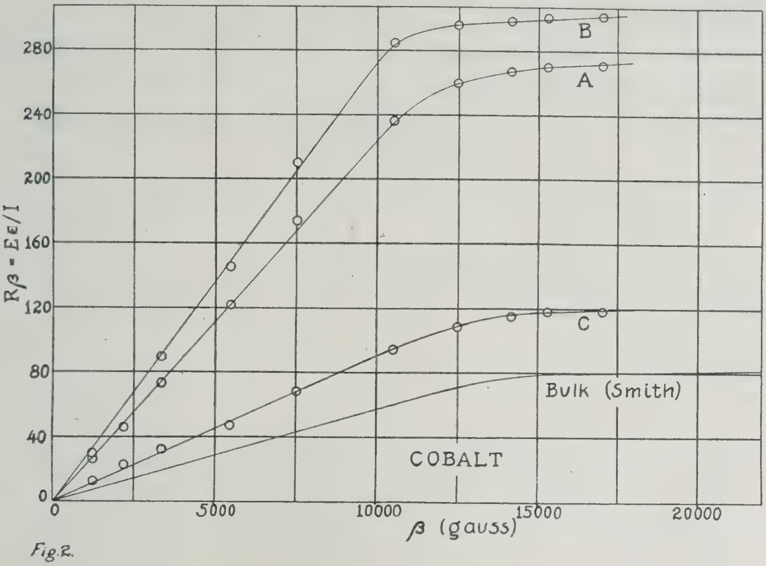

Fig. 2. Saturation of Hall e.m.f. and effect of heat treatment in evaporated cobalt. *C* is for a film heated at a higher temperature.

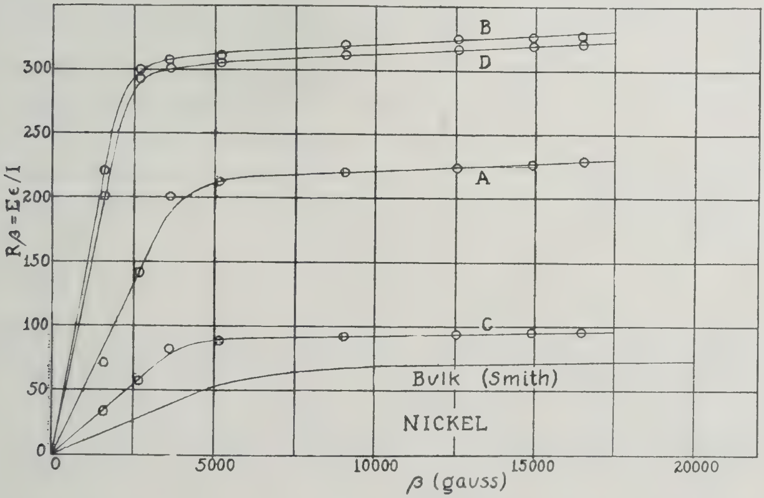

Fig. 3. Saturation of Hall e.m.f. and effect of heat treatment in evaporated nickel. *A* and *C* are for films heated at a higher temperature.

Curves E' and F' are for the same films as *E* and *F*, respectively, taken after heating F' to the softening point of glass and E' to approximately 100°C less.

The second effect of heating shown in these curves is a shift in the magnetic induction necessary to produce saturation. This effect is evidenced only in nickel and cobalt although the effect may be true for iron as well. In the heated films, *C* for cobalt and *A*, *C* and *F′* for nickel, it is evident that the value of the saturating induction is approaching that shown by Smith for bulk metals.

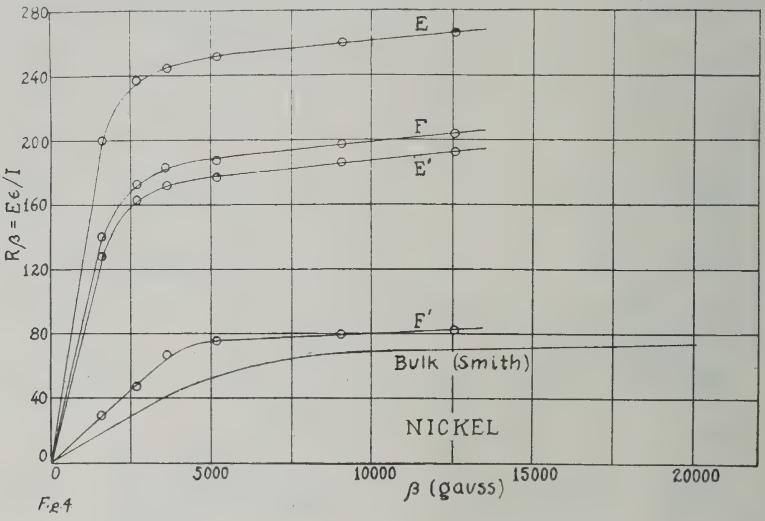

Fig. 4. Saturation of Hall e.m.f. and effect of heat treatment in evaporated nickel. *E′* and *F′* are the same films as *E* and *F* after heating.

Microscopic study. Several of the nickel and cobalt films were examined microscopically for crystal structure. Cobalt films were etched with picric acid and alcohol and nickel films with nitric acid and alcohol. At a magnification of about 300, evidence of structure was observed both by transmitted and by reflected light. Before etching, the films appeared quite smooth with no trace of crystal boundaries.

Discussion of Results

An interpretation of the above results should be based on a consideration of the probable physical state of evaporated films. Langmuir[11] has suggested the possibility of forming by evaporation either amorphous or crystalline metals depending on the temperature of the surface of condensation. This view is confirmed by the ultramicroscopic investigation of Reinders and Hamburger[12] in which they observed crystal growth in evaporated metal films in changing from liquid air temperature to

[11] I. Langmuir, Am. Chem. Soc., J**38**, 2221 (1916).

[12] Reinders and Hamburger, K. Akad. Amsterdam, Proc. **19**, 958 (1917); *ibid.* **20**, 1135 (1918).

room temperature. They were unable to obtain silver without crystalline structure but tungsten formed a deposit at the temperature of liquid air which could not be resolved. At room temperature, all of the films showed structure. Since the films of the present investigation were all deposited at temperatures considerably above room temperature, they were probably crystalline, a conclusion which is supported by microscopic examination. Three possible ways in which these films may differ from bulk metal are suggested. (1) The observed effects of heating indicate that the crystalline grains may be smaller; (2) since the films were not worked, the material between the crystals may be more porous and spongy, consisting possibly of amorphous metal or of very minute crystals with actual gaps between; (3) because of the method of deposition, the crystalline grains of the films may differ in structure from those of the metal in bulk. The observed results will now be discussed with these ideas in mind.

The high specific resistances found in the present study are in agreement with the results of Weber and Oosterhuis[2] and of Steinberg.[1] Also in the investigation of Reinders and Hamburger[12] referred to above, it was found that increasing crystal size was accompanied by a decrease of resistance which agrees with the results of the heat treatment of iron, cobalt and nickel. Thompson[13] has shown in an investigation on bulk iron that the resistance becomes smaller as the crystals are made larger by annealing. These results seem to lead to the conclusion that the high specific resistance in these evaporated films is due in part to smaller crystalline grains. The heating may also affect a difference in the material between the grains.

An explanation of the mechanism of resistance, which might come under the third possible difference listed above, is suggested by Höjendahl[14] who attempts to explain certain conduction phenomena on the basis of the rotation of the elliptic orbits of the valence electrons. This suggests a need of x-ray and optical investigation of these films.

Greater difficulty is encountered in explaining the Hall effect phenomena because the difference between the Hall coefficients for evaporated films and for metals in bulk are of opposite sign for the ferromagnetic and non-ferromagnetic elements. On the basis of the belief that the crystalline grains are smaller and in less intimate contact in the evaporated films than in bulk, the low Hall coefficients for the non-ferromagnetic metals may be quite well accounted for by assuming that only the crystalline grains contribute to the Hall effect, and that the measured

[13] F. C. Thompson, Phil. Mag. **31,** 357 (1916).

[14] K. Höjendahl, Phil. Mag. **48,** 349 (1924).

current through the film is carried to a larger extent by the gaps between the grains than in bulk, making the current through the crystalline grains themselves smaller than the measured value. Since $R=E\epsilon/\beta I$, using a current which is too large would have the effect of decreasing the value of R. With the exception of this error in the value of the current, one should expect the same R for the same material.[15] A further test of the effect of small crystalline grains might be made by thorough heat treatment of these films, if we may assume that high temperature promotes crystal growth.

In the ferromagnetic metals, the situation is evidently quite different, for, as has been shown, the Hall coefficients for evaporated films are considerably larger in absolute value than for the metals in bulk. If the above explanation is valid for the non-ferromagnetic metals, there must be a similar effect in iron, cobalt and nickel, which is hidden by a greater effect in the opposite direction. That this latter effect is closely related to ferromagnetism is evidenced by the fact that nickel, in spite of its negative Hall effect, behaves in a manner similar to iron and cobalt; however, it is difficult to conceive of a change in magnetic properties that would produce the greatest changes in nickel, the least ferromagnetic of the three. That there are differences in the magnetic properties of these films is seen from a consideration of Sorensen's[3] results, but no specific correlation with the present results is suggested.

It seems from the above considerations that there must be some fundamental change in the Hall effect in the separate crystalline grains to account for the observed results on iron, cobalt and nickel. An alteration of the atomic fields of force by some distortion of the crystalline grains or other asymmetry resulting from the conditions of deposition may offer a possible explanation.

The present results on the saturation of the Hall e.m.f. might seem to indicate a lack of proportionality between the Hall effect and the intensity of magnetization in iron, cobalt and nickel as found for these metals in bulk by DuBois[16] and Kundt.[17] This is not a necessary conclusion, however, since no magnetic measurements have been made on thin films magnetized normally to the plane as in Hall effect measurements. Inasmuch as H must be small, on account of the demagnetizing effect in a thin film, β is probably nearly equal to $4\pi I$, but the actual relation is unknown.

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[15] G. W. Stewart, Phys. Rev. **17,** 232 (1921).

[16] H. G. J. DuBois, Ann. d. Physik **31,** 491 (1887).

[17] A. Kundt, Ann. d. Physik **49,** 257 (1893).

Smith's[8] results on the variation of the Hall effect with temperature should be noted. The Hall coefficients with increasing temperature increased for the ferromagnetic metals and decreased for the non-ferromagnetic metals. This is similar to the above results. Also, he observed a similar decrease in the value of the magnetic induction necessary to produce saturation of the Hall e.m.f. in the ferromagnetic metals.

The average values of the Hall coefficients for evaporated iron, cobalt and nickel are 1.4, 4.9 and 7.8 times, respectively, the values for the metals in bulk. The magnetic induction necessary to produce saturation of the Hall e.m.f. is for nickel about 60 percent lower than in bulk, for cobalt about 8 percent lower and for iron only slightly lower. These results seem significant when we consider that in both cases these variations are in the order of the atomic number of these elements and may indicate some fundamental relation to atomic structure. If the increase in the Hall effect is due to an asymmetry in the crystals, then there is a causal atomic change related to the increase in atomic number.

In conclusion, the writer wishes to express his appreciation to the members of the Department of Physics of the State University of Iowa for their assistance and interest, and especially to Professor G. W. Stewart under whose direction the work was carried on.

PHYSICAL LABORATORY,
UNIVERSITY OF IOWA.
December 23, 1925.

NOTE ON THE MAGNETIC PROPERTIES OF RARE EARTH OXIDES

By E. H. Williams

Abstract

The *magnetic susceptibility* of three very pure rare earth oxides, namely those of cerium, holmium and praseodymium, have been measured and found to be 0.14×10^{-6}, 229×10^{-6}, and 13.4×10^{-6} dyne cm per gm respectively. The spectroscopic and atomic weight analyses for the purity of one of the elements have been checked by magnetic susceptibility measurements. The latter were found to be in good agreement with the former.

Resolution numbers obtained from a theory based by Jakob Kunz on the anomolous Zeeman effect have been compared with magnetic susceptibilities obtained by the author in this and previous papers and found to be consistent therewith.

THE scarcity of rare earths of very high degree of purity renders it desirable to make magnetic measurements on them when once they are obtained. For several years B. S. Hopkins of the Chemistry Department of this university, together with his assistants and students, has been engaged in the purification of rare earth elements and in chemical measurements upon their compounds. In previous articles[1] the author described the results of magnetic susceptibility measurements on some rare earth oxides at both high and low temperatures. Since the time of the above measurements the oxides of three more elements, namely, cerium, holmium and praseodymium, have been obtained in a very high state of purity.

The Curie balance method employed was the same as that used in the previous measurements. No attempt was made to vary the temperature, all measurements being made at room temperature and reduced to 20°C by applying Curie's law for paramagnetic substances. In no case did the room temperature differ by more than two or three degrees from 20°C.

Table I

Magnetic susceptibilities

Temperature, 20°C.

Substance	$\chi\times10^6$ dyne cm/gm
Cerium oxide	0.14
Holmium oxide	229.0
Praseodymium oxide	13.4

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[1] E. H. Williams, Phys. Rev. **12,** 158 (1918); **14,** 348 (1919).

The results for the magnetic susceptibility per gram for the three oxides are shown in Table I. The purity of each of the oxides was 99.5 percent or better.

In the first paper referred to above the author pointed out that when only two substances are involved the magnetic test is reliable in the analysis of substances. About the time the above measurements were being made, Dr. John Wierda of the Department of Chemistry was determining the atomic weight of praseodymium. To check the spectroscopic and atomic weight analyses which he was making, magnetic susceptibility tests were made. Samples of praseodymium oxide at successive stages in the process of purification were measured. The results are shown in Table II.

TABLE II

Magnetic susceptibility of samples of praseodymium oxide

Sample	$\chi \times 10^6$ dyne cm/gm
No. 23	9.3
No. 24	13.26
No. 25	13.23

These magnetic values indicate that sample No. 24 was as pure as sample No. 25. Atomic weight and spectroscopic tests gave the same results.

In a theory soon to be published Jakob Kunz arrives at certain numbers which give the resolution in the Stern and Gerlach experiment, i.e., the number of atomic beams which one would expect on the basis of the anomalous Zeeman effect. This resolution number is intimately connected with the magnetic susceptibility. In order to test this theory, the numbers that apply to the rare earth elements measured in this and the two previous papers are compared with the corresponding values of susceptibility in Table III.

TABLE III

Substance	Resolution No.	$\chi \times 10^6$dyne cm/gm (20°C)
Lanthanum oxide	4	−0.4
Yttrium oxide	4	0.53
Cerium oxide	9	0.14
Samarium oxide	9	6.0
Praseodymium oxide	12	13.4
Neodymium oxide	13	29.6
Gadolinium oxide	13	130.1
Erbium oxide	21	189.0
Dysprosium oxide	21	234.0
Holmium oxide	22	229.0

In general it is seen that there is good proportionality between the resolution number obtained by Kunz and the magnetic susceptibility values found by the author. The discrepancies may be due to the fact that the oxides were used instead of the elements.

The fact that, in the theory of Kunz, the resolution numbers of the atom for some of the rare earth elements are larger than those of any other elements gives special significance to their magnetic properties. The resolution numbers of erbium, dysprosium and holmium are more than twice that of iron and therefore we should expect these elements in the pure state to have very high magnetic susceptibilities. Thus far it has been impossible to obtain any of these elements in the pure state and thus to test this part of the theory.

Physics Laboratory,
University of Illinois.
December 23, 1925.

ACOUSTIC TRANSMISSION WITH A HELMHOLTZ RESONATOR OR AN ORIFICE AS A BRANCH LINE

BY G. W. STEWART

ABSTRACT

The author's theory of acoustic transmission in a conduit with a branch line is extended to the cases of a Helmholtz resonator and an orifice attached as branches. The effect of viscosity is included in an approximate form.

Helmholtz resonator. The components of the point impedance of the branch are found to be: $Z_1=(2\omega\rho\mu)^{1/2}(\pi R^3)^{-1}L$ and $Z_2=\rho\omega/c-\rho a^2/V\omega+(2\omega\rho\mu)^{1/2}L(\pi R^3)^{-1}$, wherein $\omega=2\pi\times$frequency, ρ is density, μ, viscosity, R, radius of orifice, L, its equivalent length, a, the velocity of sound, and V, the volume of the resonator. *Experimental verification of the theory is obtained* and in addition there is found the approximate value of a simple channel equivalent in viscosity effect to the orifice of the resonator. *The serious diminution of transmission* caused by the resonator is not limited to the neighborhood of the resonance frequency but *extends over a range of two octaves.*

Orifice. The components of the point impedance of the branch are found to be the same as those of the Helmholtz resonator, but with the term containing V omitted. Experimental verification is obtained with sizes of orifices from 7 percent to 42 percent the diameter of the conduit. *The radiation from such orifices is shown to be relatively small* and thus their impedances are practically imaginary. *Transmission* in the conduit *increases* with *frequency.* Action of *orifices* in *musical instruments* is explained by the theory. Relative values of radiation and transmission are shown by computation.

THIS is a continuation of the theory of acoustic transmission with branch lines and its purpose is a detailed investigation of the cases cited in the title.

Helmholtz resonator. In the previous article[1] was deduced the general expression for transmission,

$$(P'/P)^2=[(Z_1^2+Z_1\rho a/2S+Z_2^2)^2+(\rho a Z_2/2S)^2]\times[(Z_1+\rho a/2S)^2+Z_2^2]^{-2} \qquad (1)$$

wherein P' and P refer to the actual pressure at the junction point of branch and conduit, Z_1 and Z_2 the components of the point impedance of the branch line, $Z=Z_1+iZ_2$, ρ is the density of the medium, a is the velocity of sound and S is the area of the conduit.

It was also shown that, neglecting viscosity, for the case of the Helmholtz resonator, $Z_1=0$ and $Z_2=\rho\omega/c-\rho a^2/V\omega$ in which ω is 2π times the frequency, c is the conductivity of the orifice and V is the volume of the chamber. The above general equation is then reduced to

$$|P'/P|^2=\{1+[4S^2(k/c-1/kV)^2]^{-1}\}^{-1} \qquad (2)$$

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[1] Stewart, Phys. Rev. **26**, 688 (1925).

The approximation will be made that the effect of the viscosity in the orifice is equivalent to the viscosity in a channel of length L. The equation of motion of the gas in such a channel in which the layer adhering to the wall is small in comparison with the diameter, is[2]

$$\rho\ddot{X}dx+(\tfrac{1}{2}\omega\rho\mu)^{\frac{1}{2}}\quad O/S(\dot{X}+1/\omega\cdot\ddot{X})dx=\rho a^2\partial^2X/\partial x^2dx \tag{3}$$

Herein O is the perimeter, S is the area, μ is the coefficient of viscosity, and dx is the element of length of the tube. On the basis of assumption already stated the velocity at a distance from the walls may be regarded as $\dot{X}/S$. For a channel as short as here supposed, $\dot{X}$ may be regarded as the same throughout the length L at any instant, and consequently $\ddot{X}$ and $\partial^2X/\partial x^2$, which are proportional to X in a tube of constant cross-section, may be also regarded as similarly constant. After integrating over L, dividing by S, and substituting the values of O and S in terms of the radius R, the following is obtained

$$\begin{aligned}\left[\rho L/S+(2\omega\rho\mu)^{1/2}(\pi R\omega)^{-1}L\right]\ddot{X}+(2\omega\rho\mu)^{1/2}(\pi R^3)^{-1}L\dot{X}\\ =\rho a^2\partial^2X/\partial x^2\cdot L/S\ .\end{aligned} \tag{4}$$

From the fundamental equations of plane waves, $\rho a^2\partial X/\partial x=-S\partial p/\partial x$, p being pressure, and consequently the right hand member is the difference in pressure acting on the mass in the channel. This is $P'-\rho a^2X/V$, if X is the inward displacement into a Helmholtz resonator of volume V for the pressure exerted on the capacitance is $\rho a^2X/V$. Since $\rho L/S$ is really the inertance of the channel, it should be replaced by ρ/c of the actual orifice. When these substitutions are made and the relationship $\ddot{X}=i\omega\dot{X}=-\omega^2X$ is applied, there results,

$$\begin{aligned}\{(2\omega\rho\mu)^{1/2}(\pi R^3)^{-1}\cdot L+i[\rho\omega/c-\rho a^2/V\omega+(2\omega\rho\mu)^{1/2}\\ \times(\pi R^3)^{-1}\cdot L]\}\dot{X}=P'\end{aligned} \tag{5}$$

The coefficient of $\dot{X}$ is the impedance of the resonator and consequently we may write at once the values,

$$\begin{aligned}Z_1&={}^{/2}((2\omega\rho\mu)^1\pi R^3)^{-1}\cdot L\ ,\\ Z_2&=\rho\omega/c-\rho a^2/V\omega+(2\omega\rho\mu)^{1/2}\cdot L(\pi R^3)^{-1}\ .\end{aligned} \tag{6}$$

If the values of Eq. (6) be now substituted in Eq. (1), the transmission can be computed for any frequency. Z_1, upon which dissipation obviously depends, vanishes with μ as would be anticipated. Z_2 depends upon the inertance and capacitance of the resonator, and the effect of viscosity is virtually an addition to the inertance or the subtraction from the capacitance of a function varying with ω and μ.

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[2] Rayleigh, Theory of Sound, Vol. II, §347, Eq. (10).

The orifice. If there is an orifice without the resonator, the correct expression for the pressure acting on the mass in the channel is no longer $(P'-\rho a^2X/V)$ but $(P'-\rho(k^2a/2\pi)\dot{X})$ where the second term in the latter[3] is the dissipative force at the opening. Making this substitution in (4) and proceeding as before, there is obtained

$$\{\rho k^2a/2\pi+(2\omega\rho\mu)^{1/2}(\pi R^3)^{-1}\cdot L+i[\rho\omega/c+(2\omega\rho\mu)^{1/2} \times(\pi R^3)^{-1}\cdot L]\}\dot{X}=P' . \tag{7}$$

Thus,

$$Z_1=\rho k^2a/2\pi+(2\omega\rho\mu)^{1/2}(\pi R^3)^{-1}\cdot L ,$$
$$Z_2=\rho\omega/c+(2\omega\rho\mu)^{1/2}(\pi R^3)^{-1}\cdot L . \tag{8}$$

Thus, dissipation depends upon both viscosity and radiation, while the inertance is affected by the presence of viscosity. The values of Eq. (8) may now be substituted in Eq. (1) and the transmission computed for any frequency.

Experimental and theoretical results. The circles on the plot of Fig. 1 show the experimental values of $|P'/P|^2$ as taken by an ear comparison method of intensity measurement[4] which is sufficiently accurate for the present purpose. In computing the theoretical results, the only uncertainty is the selection of the value c, for the conductivity of the orifice. Were it an orifice in an infinite plane wall, we have given the well-known theoretical[5] inferior and superior limits for the corrections to the length of one end of the channel; namely $.785R$ and $.85R$. But it is known that the correction without a flange is distinctly less, approximately $.6R$. The correct value for the present cases of an opening in a tube with or without a chamber, is not known and therefore must be selected. The writer has somewhat arbitrarily chosen the inferior theoretical flange value, $.785R$, making the total correction of length $2\times.785R$ or $\pi R/2$. The error will not be great and can be ascertained by later experimental refinements. The value of c is thus $\pi R^2/(L+\pi R/2)$.

The curve drawn in Fig. 1 has been computed in accord with Eq. (1) with the values of Z_1 and Z_2 given by Eqs. (6). It is found by trial that for any value of L comparable to the length of the orifice, the curve is not altered by assuming $\mu=0$ or by using (2). The dotted curve with ordinates designated on the right shows the computed response of the same Helmholtz resonator in the open with a source of sound producing a pressure P at the resonator when the orifice is closed. If the internal variation of pressure is G, the ordinates represent[6] $|G/P|^2$ and indicate the sharpness of response of such a resonator as ordinarily used.

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[3] Rayleigh, Theory of Sound, Vol. II, §311.

[4] The method used is really an improvement of that discussed in the Phys. Rev. **20**, 528 (1922), and will be described in a later article.

[5] Rayleigh, Theory of Sound, Vol. II, 183.

Fig. 2 is similarly prepared for the case of a small orifice, the chamber being reduced in size also so that the computed minimum transmission without viscosity is at approximately the same frequency as in Fig. 1. Curve a is the theoretical curve omitting viscosity and curve b the computed one using the values given in Eq. (6), assuming $\mu = .00018$ and $L = .09$ cm or six times the actual length of the orifice.

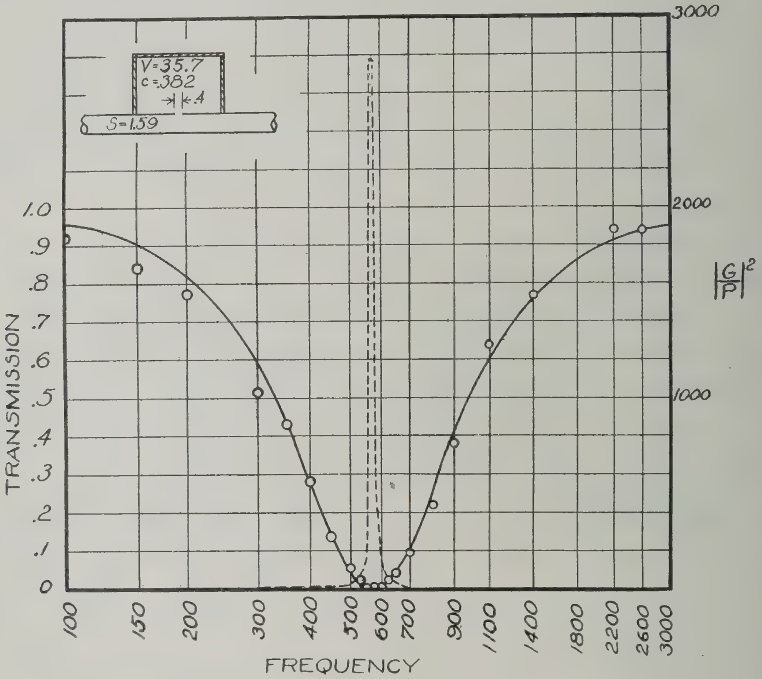

Fig. 1. Helmholtz resonator as a branch.

There are several points of interest in the comparisons. First, it is noticed that the resonator seriously influences transmission for more than an octave in either direction. This is hardly to be anticipated from the sharpness of the action of the resonator as ordinarily used and as indicated by the dotted curve in Fig. 1. Second, the comparison of experiment with theory justifies the assumption of an equivalent channel as a close approximation to the effect of viscosity in the region of the frequency of minimum transmission. This experiment is, in fact, an

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[6] Rayleigh, Theory of Sound, Vol. II, §311.

$$|G/P|^2 = \left[(1-k^2V/c)^2 + (k^3V/2\pi)^2\right]^{-1}$$

approximate method of determining the equivalent length of this channel in this frequency region. Computation shows that a change of 10% in the assumed L, will produce a noticeable inferiority of agreement with experiment. Third, the comparison of theory and experiment gives entire confidence in the former. The variations from theory are probably caused by experimental inaccuracies.

Experiments with an orifice are perhaps more interesting because such cases occur frequently. Fig. 3 shows the dimensions of the orifices used, the square root of the observed transmission is indicated by marked points and the computations from theory are represented by a full line curve. The values last named are obtained by substituting the values of Z_1 and Z_2 of Eq. (8) in Eq. (1) but first assuming $\mu = 0$. If the value, $\mu = .00018$, be used, no appreciable change in the curves results, even with the smallest orifice. Curve 4, Fig. 3, does not agree with the observed points and this is doubtless because, as the orifice becomes larger, the value of c is less and less approximately the value for the orifice opening into an infinite plane. If its value is increased arbitrarily to 0.74, the agreement with observations is satisfactory. Obviously there is here suggested a method of measuring c. It should be mentioned that this experimental value of 0.74 proves to give agreement of theory and experiment in the case of a Helmholtz resonator as a branch having the same orifice. In order to test the influence of radiation from the orifice into the open, the value of Z_1, Eq. (8), is placed equal to zero in Eq. (1).

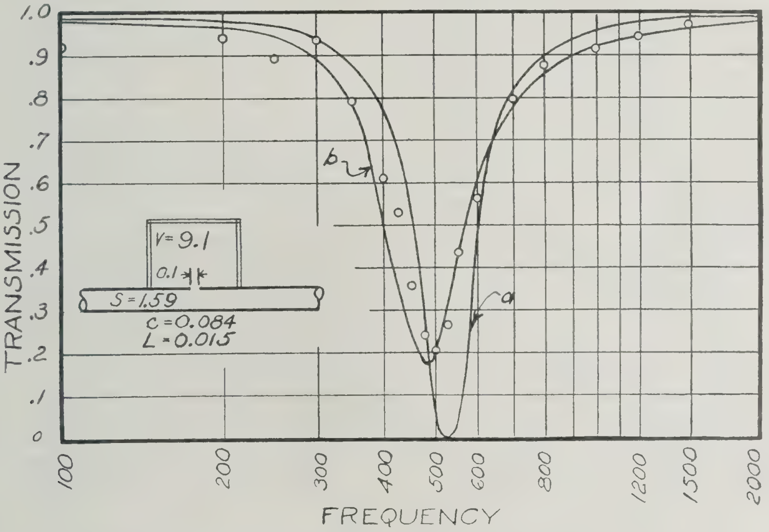

Fig. 2. Effect of viscosity in the orifice.

The resulting changes in the lowest curve are shown by the dotted curve in Fig. 4. This is the case of the largest orifice. *The change is surprisingly small.* It should be stated that in the theory the radiation is assumed to occur from a hole in an infinite plane wall, an approximation not unsatisfactory because of the small amount of radiation. Fig. 4 also shows the data and computations at higher frequencies using the largest orifice.

The above comparisons of theory and experiment present several points of interest. First, orifices in a conduit diminish transmission with a magnitude increasing with decreasing frequency. Second, neither viscosity nor radiation seriously influences the value of transmission in the cases cited. Third, the diminution in transmission is not caused by a loss of energy but by the inertance of the orifice which produces a reflected wave.

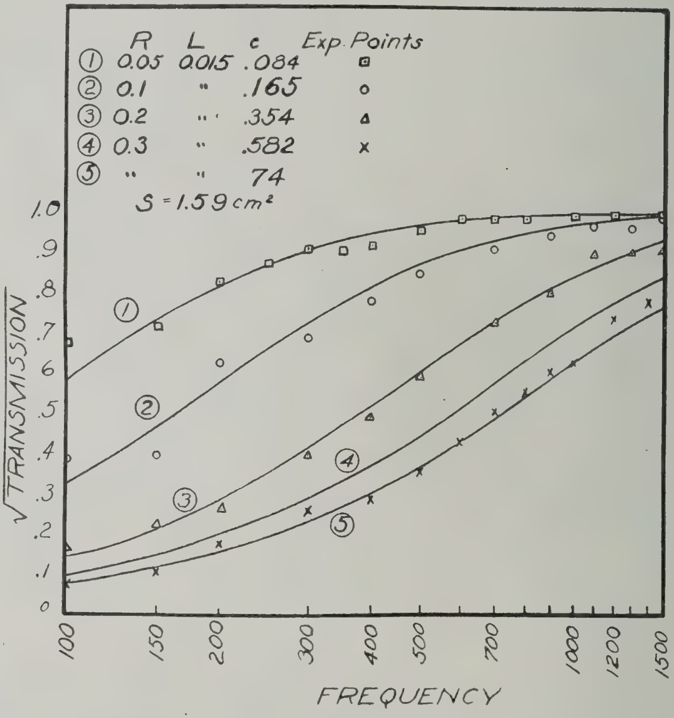

Fig. 3. Orifices as branches of a conduit.

While the foregoing refers to a wave transmitted in one direction, the general effect produced in a resonant musical instrument can be understood. Consider the opening of a key on a clarinet. There is a reflected wave from the opening, as if it were an open end of a pipe and this condition, as is well known, enables the *resonant* tone for that pipe length to be established. The intensity of the incident wave becomes very large and consequently the sound escaping from the bell of the clarinet is made sufficiently large. Thus it is noticed that most of the sound escapes from the bell of the clarinet and not from the orifice. This wave reflected from the orifice would be a detriment to the establishment of any tone not in resonance. The radiation from the hole is small in comparison with the transmission along the tube and subsequent radiation from the bell. This phenomenon may be explained in the following terms: the impedance of an orifice is approximately, but not entirely, imaginary, and hence practically wattless, whereas the impedance of an infinite pipe or conduit is real and has no wattless component. A number of years ago Boehm[7] noted that the transmission along the axis of the flute was much greater than through an orifice having an area as large as the cross-section of the conduit. The above discussion supplies the explanation.

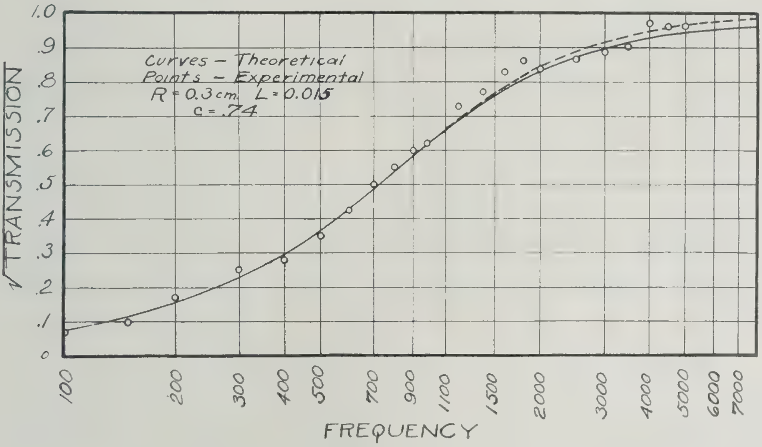

Fig. 4. Difference in transmission caused by radiation.

I wish to acknowledge the valuable assistance of Mr. W. D. Crozier in these experiments.

Department of Physics,
University of Iowa,
January 5, 1926.

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[7] Theobald Boehm, "On the Flute," translated and published by D. C. Miller. See p. 25.

THE TUBE AS A BRANCH OF AN ACOUSTIC CONDUIT: THE SPECIAL CASE OF THE QUINCKE TUBE

By G. W. Stewart

Abstract

The author's theory of acoustic transmission in a conduit with a branch line is extended by obtaining the thoretical values of the components of the point impedance of a closed and of an open tube.

The branch an open tube. The components of the impedance of the branch are $Z_1=(\rho\omega k/2\pi)D^{-1}$ and $Z_2=\rho\omega/c_0+[\rho\omega/k\sigma\cdot \sin kl \cos kl+\rho\omega/c\,(\cos^2 kl-\sin^2 kl)-k\sigma\rho\omega(k^2/4\pi^2+1/c^2)\sin kl \cos kl]D^{-1}$, wherein $D=k^2\sigma^2(k^2/4\pi^2+1/c^2)\sin^2 kl+\cos^2 kl-2k\sigma/c \sin kl \cos kl$, ρ is the density, $\omega=2\pi\times$ frequency $=k\times$(sound velocity), c_0 and c are the conductivities of the conduit orifice and distant orifice respectively, σ is the area and l is the length of the tube. These values of impedances are used in computing the transmission through the conduit in accordance with fundamental theory (Phys. Rev. **5,** 26, 688 (1925)). A comparison with experiment shows agreement. The transmission when the tube is at resonance is very different from the case of the same orifice without the tube.

The branch a closed tube. The above values of impedance reduce to $Z_1=0$, and $Z_2=\rho\omega/c_0-\rho a/(\sigma \tan kl)$. The theory of transmission thus established is that of the Quincke tube. The selectivity is not sharp as is the cylinder in the open, the effect being marked over a total range of an octave. The effect of viscosity in increasing the minima of transmission is shown.

The branch an impedance of any kind. If the point impedance of the attachment be known, then to its imaginary component may be added $\rho\omega/c_0$ and both components used in the original formula for transmission. Also if such an attachment is by means of a tube of constant cross section, the theory will give the transmission.

Theory

The theory previously established for the influence of branch lines on acoustic transmission[1] shows that the ratio of the energy flow in the transmitted wave to that in the incident wave is

$$[(Z_1^2+Z_1\rho a/2S+Z_2^2)^2+(\rho a Z_2/2S)^2][(Z_1+\rho a/2S)^2+Z_2^2]^{-2}.$$

Here ρ is the density of the medium, a the sound velocity, S the area of the conduit and Z_1 and Z_2 are the components of the point acoustic impedance $Z=Z_1+iZ_2$, defined as the ratio of the excess pressure and the volume-current, all three quantities being regarded as complex. The computed values depend upon a knowledge of Z_1 and Z_2. The purpose of this contribution is to establish the expression for the values of Z_1 and Z_2 for any length of tubular side branch, open or closed, and in fact for any attachment, the point impedance of which is known, connected to the conduit by a tube of constant cross-section.

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[1] Stewart, Phys. Rev. **26,** 688 (1925).

Consider a tube of diameter small in comparison with a wave-length, making the wave front perpendicular to the axis. Let the displacement be ξ, positive with the axis x of the tube. It can then be shown[2] that, in case of a simple harmonic vibration:

$$\partial^2 p/\partial x^2 + \partial/\partial x\,(\log\sigma)\cdot\partial p/\partial x + k^2 p = 0 \tag{1}$$

$$\partial^2\xi/\partial x^2 + \partial/\partial x\,(\log\sigma)\cdot\partial\xi/\partial x + \partial^2/\partial x^2\,(\log\sigma)\cdot\xi + k^2\xi = 0 \tag{2}$$

wherein p is the pressure, k is 2π divided by the wave-length, and σ is the area of the tube.

The solutions of the equations take the form[2]

$$p_2 = a'p_1 + b'X_1\,, \qquad X_2 = c'p_1 + d'X_1 \tag{3}$$

wherein the subscripts, 1 and 2, refer to the open ends of the tube at x_1 and x_2, $x_2 > x_1$, X is $\sigma\xi$, or the volume displacement, and a', b', c' and d' are constants the general values of which are indicated by Webster.[2] Eq. (3) may be written in terms of X_1 and then from the two may be obtained the following:

$$Z_1' = p_1/\dot{X}_1 = (i\omega Z_2'd' - b')(c'\omega^2 Z_2' + i\omega a')^{-1}\,. \tag{4}$$

Herein Z_1' and Z_2' are complex impedances defined by $Z_1' = p_1/\dot{X}_1$ and $Z_2' = p_2/\dot{X}_2$. Assuming a cylindrical tube, σ is constant, and Webster's values of the constants become: $a' = d' = \cos kl$, $b' = (\beta/\sigma)\sin kl$, $c' = -(\sigma/\beta)\sin kl$, if β is written for $\rho a^2 k$. Eq. (4) then becomes

$$\begin{aligned} Z_1' = (\beta/\sigma)\,&[i\omega Z_2'\cos kl - (\beta/\sigma)\sin kl] \\ &\times [i\omega(\beta/\sigma)\cos kl - \omega^2 Z_2'\sin kl] \end{aligned} \tag{5}$$

If the attachment of the tube to the conduit be at x_1, then Z_2' is the point impedance of the other end, x_2. Eq. (5) then gives the point impedance of the tube for any attachment at its terminus, if the point impedance of the attachment, Z_2', is known. In the actual arrangement here discussed, there should be added to Z_1', the inertance of the orifice into the conduit. As shown in an earlier paper,[3] this is $\rho\omega/c_0$, the subscript of c_0 being used to distinguish it from the conductivity of the open end.

If the distant end of the tube is open, the value of Z'_2 is that of an orifice,[3] $(\rho k^2 a/2\pi + i\rho\omega/c)$, wherein a is the velocity of sound and c is the conductivity of the orifice.

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[2] For example see A. G. Webster, Proc. Natl. Acad. Sci. **5**, 275–282 (1919), Eqs. (21), and the solutions Eq. (24).

[3] Stewart—preceding paper in this issue. In Eq. (8), if $\mu = 0$, the value quoted in second reference follows by adding Z_1 and iZ_2.

When to Eq. (5) there is added $\rho\omega/c_0$ and there is inserted the value of Z_2' for the open end, the following components of impedance are readily found:

$$
\begin{aligned}
Z_1 &= (\rho\omega k/2\pi)D^{-1} \\
Z_2 &= \rho\omega/c_0 + \Big[\rho\omega/k\sigma \cdot \sin kl \cos kl + \rho\omega/c(\cos^2 kl - \sin^2 kl) \\
&\qquad - k\sigma\rho\omega\left(\frac{k^2}{4\pi^2}+\frac{1}{c^2}\right)\cdot \sin kl \cos kl\Big] \times D^{-1}
\end{aligned}
\tag{6}
$$

if
$$
D = k^2\sigma^2\left(\frac{k^2}{4\pi^2}+\frac{1}{c^2}\right)\sin^2 kl + \cos^2 kl - \frac{2k\sigma}{c}\sin kl \cos kl\ .
$$

If the cylinder is closed, $Z_2' = \infty$, $Z_1' = -(i\rho a/\sigma)\cot kl$, and

$$
Z_1 = 0\ , \quad \text{and } Z_2 = \rho\omega/c_0 - \rho a/(\sigma \tan kl)
\tag{7}
$$

It is to be observed that in obtaining Eqs. (6) the value of Z_2' was obtained as if the cylindrical tube opened into an infinite plane. Any attachment whatever can be made at this point and, if its point impedance is known equations corresponding to (6) can be obtained by appropriate substitution of Z_2' in Eq. (5).

Given the values of Z_1 and Z_2 in any case, the substitution may be made in the value of the transmission given in the first paragraph. The selection of the values of c_0 for the entering orifice of the conduit and of c for the other end is a matter of judgment as experimental knowledge is lacking. In a previous article[3] it was explained that the correction to the length at the conduit end would be made $.785R$ or $c_0 = 4R$. Inasmuch as experimental values of the correction[4] for the open end average about $.57R$, the conductivity of the open end would be $c = \pi R^2/.57R = 5.5R$. These two values will be used in the computations.

EXPERIMENTAL RESULTS

As illustrative of the application of the equations, the experimental results for the closed and the open tube will be shown.

Fig. 1 shows the square root of the transmission in the case of the closed tube. The points represent observations made by an ear comparison method previously described,[4] and the full line represents the computations using the values of Eq. (7) in the expression

$$
[(Z_1^2 + Z_1\rho a/2S + Z_2^2) + (\rho a Z_2/2S)^2]^{1/2}[(Z_1 + \rho a/2S)^2 + Z_2^2]^{-1}
$$

or the square root of the transmission. The difference is two-fold. First, the experimental curve does not have a minimum of zero. This is probably caused by dissipation through viscosity. Second, the computed points are displaced toward smaller frequencies. This is accounted for by our consistent adherence to the value of $c_0 = 4R$. It is obvious that,

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[4] See Barton, Text Book of Sound, p. 251.

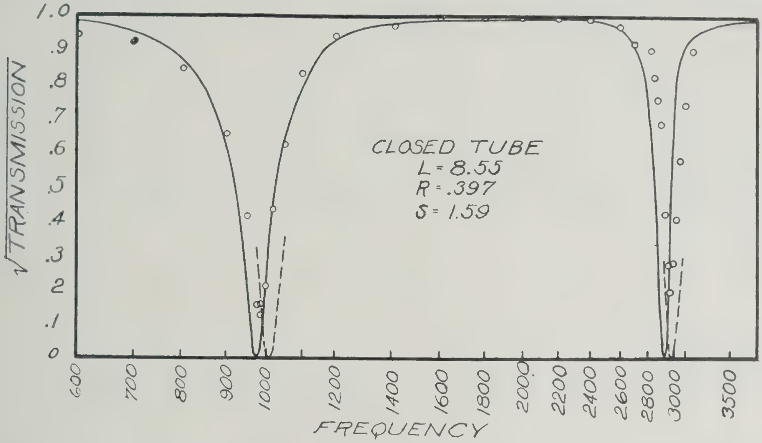

Fig. 1. The closed tube as a branch.

although this value may be satisfactory where the orifice into the branch is small in comparison to the area of the conduit, yet in the present case it cannot be a correct value, for the end does not open out into free space.

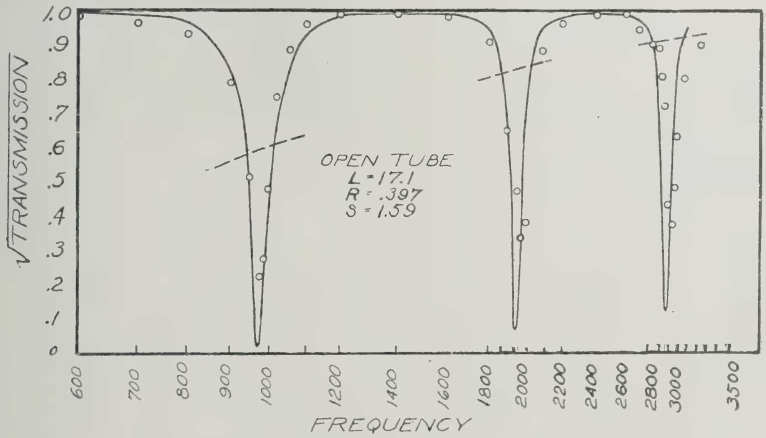

Fig. 2. The open tube as a branch.

In this value of c_0 must be acknowledged an unavoidable approximation. The dotted minima indicate the computations with $c_0 = \infty$. Undoubtedly viscosity accounts for the increase with frequency of the transmission at the minimum. The variation between experiment and theory is sufficiently small to indicate the essential accuracy of the theory.

Fig. 2 shows the case of an open tube approximately twice as long as the closed tube in Fig. 1. The effect of viscosity should be greater and in addition there is radiation. The curves seem to verify this. The dotted line shows what would be expected if l were zero. It is obvious that it does not and should not give the same transmission as that at the minimum with the resonating tube. The minima increase with frequency, indicating an increased radiation and increased viscosity. Comments concerning the value of c_0 would be similar to those just given in regard to Fig. 1.

QUINCKE'S TUBE

It is evident that this theory of the closed cylinder covers the case of a Quincke tube which is merely a side tube that decreases transmission at its resonance frequency. Without viscosity the reduction is complete irrespective of the diameter of the branch, but in practice it is necessary to use several branches[5] in order to reduce this resonance frequency to inaudibility. The results of both theory and experiment in Fig. 1 indicate the effectiveness of such a Quincke tube and its range of selectivity. When using more than one such tube in the branch, it is necessary to place them one-half wave-length apart, for then the destructive waves from them agree in phase. It is not necessary, as Kreuger[6] states, to place them at any fixed distance from the source provided there is sufficient damping to prevent the backward waves from influencing the source.

I wish to acknowledge the valuable assistance of Mr. W. D. Crozier in these experiments.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF IOWA,
January 5, 1926.

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[5] The method used is really an improvement of that discussed in the Phys. Rev. **20**, 528 (1922), and will be described in a later article.

[6] Kreuger, Philos. Stud. **17**, p. 223, (1901).

APRIL, 1926 PHYSICAL REVIEW VOLUME 27

THE DURATION OF THE TRANSIENT STATE IN THE SETTLING OF SMALL PARTICLES

By Warren Weaver

Abstract

The general theory of the settling of small particles in a fluid is used to determine an upper limit for the time required to establish the steady, exponential distribution of density. It is shown that the steady state will, in in any case in which the initial distribution of particles is uniform, be sensibly attained in that length of time required by one of the particles, moving with the velocity given by Stoke's law, to fall two tube lengths. An examination of Burton's experiment (which sought to prove that the exponential distribution law holds for only very small depths below the surface) indicates that the steady state should have been reached in about 37 days. His failure to find any evidence of an exponential distribution of density after 50 days cannot be ascribed to an inadequacy in the time allowed for settling.

SMALL particles immersed in a fluid in such numbers as to form a dilute suspension experience a steady gravitational drift, the velocity of which is given by Stoke's law of fall, and a Brownian movement due to molecular bombardment. If no other effects such as, for example, electrical or thermal, are present, the two mentioned motions finally produce (whatever be the initial distribution of particles in the fluid) a distribution characterized by the exponential law

$$n=n'e^{\frac{N}{RT}X(x-x')},$$

where n is the number density of particles at a position x, the density at x' being n'; where N is Avagradro's number, R the gas constant for a gram molecule, T the absolute temperature, and X the gravitational force acting on one of the particles.

It has been suggested by Burton[1] that this exponential distribution is merely a surface phenomenon, in the sense that the above law holds for only very small distances below the surface of the liquid. This contention was based upon the fact that the law had been tested (notably in the well-known work of Perrin) only for small depths, and upon Burton's belief that the law leads to density ratios, when a difference in depth of several centimeters is considered, which are not in accord with physical common sense or experience. Burton therefore experimented with a cell of depth 96 cm, and found, after waiting fifty days for a steady state to be established, no sensible variation of density with depth.

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[1] Burton, Proc. Royal Soc. **A. 100,** 414 (1921–22).

Two questions arise in connection with this experiment. Were effects other than the two above postulated present, and was sufficient time allowed for the steady state to be established? No discussion will be made here of the first of these questions, which has been treated in a paper by Porter and Hedges.[2] The present note gives an answer to the second question.

Consider a tube of depth l, filled with a liquid of viscosity μ, in which is immersed, at time $t=0$, a uniform distribution of number density n_0 of particles of radius a and effective density δ. Set,

$$\alpha = RT/NXl\ ,\quad \beta = 9l\mu/2g\delta a^2\ ,\quad x = yl\ ,\quad \beta t' = t.$$

It is readily checked that β is the time required for one of the particles, moving with the velocity given by Stoke's law, to fall a distance l; so that $t'=0.5$, for example, corresponds to the time in which a particle would fall half the tube length.

It has been shown[3] that the density n at a depth x at time t is given by

$$\frac{n}{n_0} = \frac{e^{y/\alpha}}{\alpha(e^{1/\alpha}-1)} + 16\alpha^2\pi e^{(2y-t')/4\alpha} \sum_{1}^{\infty} \frac{e^{-\alpha m^2\pi^2 t'} m(1 \mp e^{-1/2\alpha})\left[\sin m\pi y + 2\pi m\alpha \cos m\pi y\right]}{(1+4\pi^2 m^2\alpha^2)^2} \tag{1}$$

where the upper sign is used when m is even, the lower when m is odd. In the paper just referred to, graphs were drawn for the cases $\alpha=0.025$, 0.1, 0.3, 0.5, 2.0 and for such values of t' as would show the way in which the steady state is set up. This range of values of α was chosen so as to include the value which α had (namely, 0.475) in Perrin's work with gamboge particles. The limited information which these five families of curves afford indicates that as α decreases the time required to set up a steady state increases. This evidence is presented in Fig. 1, drawn from the curves of the previous paper. This figure shows the magnitude of the transient term for the time $t'=0.5$, for the values of α indicated, and for values of y which correspond to the lower half of the tube. It is seen that as α decreases, the transient term becomes larger. Now in the case of Burton's work $\alpha=1.95\times10^{-6}$, while $\beta=1.60\times10^{6}$. Insofar as extrapolation from so limited a range to so far removed a value is of any significance whatever, these figures would indicate, together with the above graph, that a very large time might be required for the establishment of the steady state; for the very small value of α indicates a large value of t', which, in turn, since β is large, indicates a still larger value of t. The relationship between t' and t is indicated by the fact that the time, fifty days, actually allowed to elapse, corresponds to $t'=2.7$, while the value of $t'=100$ corresponds to over five years.

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[2] Porter and Hedges, Phil. Mag. **44,** 641 (1922).

[3] Mason and Weaver, Phys. Rev. **23,** 412 (March 1924).

It is not physically evident whether decreasing α should increase or decrease the time required for the steady state to be sensibly established. Increasing l decreases α, and an increased tube length (other factors remaining the same) would naturally lead to an increased time. An increase in X, however, also decreases α and an increase in X by, say, increasing the density of the particles would seem to decrease the relative effectiveness of the Brownian movement, which tends to maintain a uniform density, as compared to the Stoke's fall.

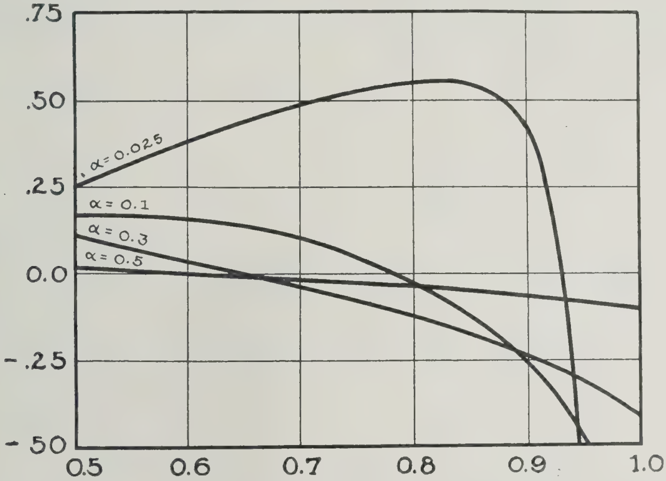

Fig. 1. The magnitude of the transient term at t′=0.5. The abscissas range from $y=0.5$ to $y=1.0$, and thus correspond to the lower half of the tube.

These considerations lead one to believe it possible that the fifty days allowed were perhaps quite inadequate for the establishment of a steady state. It therefore is desirable to determine this time from the general solution (1). For so small a value of α as characterized Burton's work, the actual calculation of the sum involved is prohibitively laborious, since many hundred terms must be used to obtain the value of n for a single value of x and t. An upper limit to the transient term may, however, be easily calculated. In fact, for any value of y,

$$\sum_{1}^{\infty} \frac{e^{-km^2}(1 \mp e^{-1/2\alpha})m \sin m\pi y}{[1+4\pi^2\alpha^2 m^2]^2} < (1+e^{-1/2\alpha}) \sum_{1}^{\infty} m e^{-km^2}$$

$$< (1+e^{-1/2\alpha}) \sum_{1}^{\infty} e^{-km},$$

the last step following from comparison of the series

$$\begin{array}{l} e^{-k}+e^{-2k}+e^{-3k}+e^{-4k}+e^{-5k}+e^{-6k}+e^{-7k}+e^{-8k}+e^{-9k}+\cdots \\ e^{-k}+0\quad+e^{-4k}+e^{-4k}+0\quad+0\quad+e^{-9k}+e^{-9k}+e^{-9k}+\cdots \end{array}$$

Moreover,

$$\sum_1^\infty e^{-mk}=e^{-k}/(1-e^{-k})\ .$$

Similarly

$$\sum_1^\infty \frac{2\pi\alpha e^{-km^2}(1\mp e^{-1/2\alpha})m^2\cos m\pi y}{[1+4\pi^2\alpha^2m^2]^2}<2\pi\alpha(1+e^{-1/2\alpha})\sum m^2e^{-km^2}$$
$$<2\pi\alpha(1+e^{-1/2\alpha})\sum me^{-km}\ ,$$

and

$$\sum_1^\infty me^{-km}=e^{-k}/(1-e^{-k})^2$$

Hence, calling the transient term $H\ (y,t')$, and identifying k with $\alpha\pi^2t'$

$$H(y,t')<16\pi\alpha^2e^{(2y-t')/4\alpha}(1+e^{-1/2\alpha})e^{-k}\left[\frac{1}{1-e^{-k}}+\frac{2\pi\alpha}{(1-e^{-k})^2}\right]\ ,$$

or

$$H(y,t')<\frac{16\pi\alpha^2(1+e^{-1/2\alpha})(1+2\pi\alpha-e^{-k})e^{\frac{2y-t'(1+4\pi^3\alpha^2)}{4\alpha}}}{(1-e^{-k})^2}$$

When α is of the order of 10^{-6}, as in Burton's experiment, and t' is not so large but that $\alpha\pi^2t'$ is also small, this reduces to

$$H(y,t')<\frac{16\alpha}{\pi t'}e^{\frac{2y-t'}{4\alpha}}\ .$$

On account of the size of α, the exponential factor decreases with enormous rapidity towards zero as soon as t' exceeds $2y$; and thus, since y never exceeds 1, as soon as t' exceeds 2. For example

t'	Upper bound for H
2.0000	5×10^{-6}
2.0001	3×10^{-11}
2.001	2×10^{-59}

Since the curves drawn in the previous article show that as α ranges from 0.1 to 2.0 the steady state is more and more rapidly attained, being sensibly reached in the slowest instance by $t'=1.0$; and since the above argument shows that for smaller values of α the steady state is sensibly attained for values of t' just exceeding 2, it is therefore possible to state in general that the steady state will in all cases be reached in that length of time necessary for one of the particles, moving with the velocity given by Stoke's law, to fall two tube lengths.

It is therefore assured that in Burton's experiment, in which $t'=2.0$ corresponds to approximately 37 days, sufficient time was allowed for the steady state to be established.

DEPARTMENT OF MATHEMATICS,
UNIVERSITY OF WISCONSIN,
January 4, 1926.

BOOK REVIEWS

The Theory of Measurements. LUCIUS TUTTLE and JOHN SATTERLY.—This text, according to the authors, is intended for undergraduate students both in mathematics and in the physical sciences. The treatment is very elementary and a minimum of mathematical knowledge (not even trigonometry) is presupposed. The book, however, includes most of the information on this subject which every graduate student in Physics, and in the other exact sciences, should have but so often unfortunately does not have. It forms an admirable introduction to the more extended accounts of special topics found in more advanced texts. The range of topics is quite remarkable, as can be gathered from a few of the twenty-two chapter headings, taken at random,—Weights and Measures, Significant Figures, Logarithms, the Slide Rule, Graphic Analysis, Interpolation and Extrapolation, Deviation and Dispersion, Least Squares, Applications to Biology. The last portion of the book is designed especially for students in the biological (and medical) sciences. Numerous problems are included with every chapter, and these with many illustrations and typical numerical results, fit it for its avowed purpose as a complete textbook on this subject.—Pp. xii+333, 93 figs. Longmans, Green and Co., New York City, 1925. Price $4.50.

RAYMOND T. BIRGE.

Helmholtz's Treatise on Physiological Optics. Volume III, The Perceptions of Vision. Translated from the third German edition. Edited by Prof. James P. C. Southall.

A goodly portion of our knowledge of the world about us may be credited directly to the human organ of vision. That organ is almost immeasurably more powerful than all the other sense organs combined. Its structure and functioning were minutely described and discussed in the first two volumes of Helmholtz's Physiological Optics. The third and final volume deals with the perceptions and impressions obtained through vision.

Now our impression of an observed object is composed of a great many different factors. These are of two classes, what is seen and what is known of this and similar objects; the retinal image, the difference between the two retinal images, muscular and nervous efforts connected with vision and the like constitute the visual function itself but this is but a small part of the story our eyes tell us, namely, our interpretation of that seen. If a stationary object be viewed and the head turned, the object is still seen stationary. If the eyes be turned from side to side it still appears stationary though its image races across the retina. It is only when the whole body or the object viewed is actually moved that motion is sensed. The retinal image is inverted but we see objects erect. If the retinal image is erected (by means of an auxiliary lens) objects are seen inverted but a week or two of continuous use is sufficient to reform the correct interpretation just as with colored glasses or spectacles in even shorter time. Even the defects of the eye, or more properly the departures from strictly orthoscopic imagery, are unconsciously allowed for. Artists, seeking to produce impressions rather than exact reproduction, must exaggerate the barrel distortion, contrasts, chromatic aberration and diffuseness from the center of attention outward in order to produce the impression sought.

Such is the nature of the field which is the subject of this third part of physiological optics. Helmholtz frankly states that the material is but fragmentary but that it is better to make a beginning. This translation is of the third German edition which is practically a reproduction of the first written by Helmholtz in 1866. The numerous notes and several appendices by von Kries follow closely the original plan. Binocular vision is treated quite fully since the invention of the stereoscope by Wheatstone had just then attracted considerable attention. Whether our concepts of space and time are intuitive or are the result of experience was much debated in those days, Helmholtz holding that our ideas of space are largely empirical and acquired. If criticism be offered such a monumental work it must be first that it is not sufficiently comprehensive in plan. Breadth and balance are lacking although a few subjects are discussed with great thoroughness. Secondly, the treatment is geometrical and philosophical rather than physical and psychological as it properly should be. A proper treatment of the field should be (inter alia) a veritable text book of the fundamental principles of art. Material is now available for filling in nearly all parts of the field attempted and even for an outline of the limitations of visual preception. The translation is excellent, clear and vivid despite the many fine distinctions drawn between concepts but roughly definable. The volume closes with a 16-page bibliography of the recent (1911–1925) literature of the subject and very full indices to both authors and subjects cited. Pp. x+736, 81 figs. Published by the Optical Society of America, and to be obtained from the Secretary, F. K. Richtmyer, Cornell University. $7.

P. G. Nutting

Modern Magnetics. Felix Auerbach. Translated by H. C. Booth.—The German edition of this work (*Modern Magnetismus*, Vieweg, Jena, 1921) is a diffuse and uncritical but very readable account of the subject down to about 1915. The arrangement is peculiar, magneto-optics, for an example, preceding electro-magnetic theory. What little mathematics is attempted suffers from the author's bias for graphics and from an unsystematic choice of symbols (q stands for four different things besides being the abbreviation for "curl"). There are a few bad blunders, notably in regard to the equipotential surfaces for a separated pair of unlike poles of equal strength (Figs. 4 and 9, with associated text). The present translation is neither good English nor a fair equivalent for the original German, and contains many absurdities. The specialist can guess from the context that "developed" (p. 199) should be "wound with wire," and that "beam" (p. 133) should be "radiation," but the unwary reader will go astray at least once on every page. The unfitness of the translator may be judged from his invention of the clause (p. 192): "when the permeability of iron becomes small in comparison with that of air." The index is poor. The publisher is to blame for now issuing as "modern" a book which barely deserved that adjective five years ago. The condensation of the table of contents is unfortunate, because the remaining chapter titles are none too descriptive. The cuts contain all the original imperfections (Figs. 65, 74), the half-tones are foggier (Fig. 87) and the new lettering is often slovenly (Figs. 52, 59). A commendable change is the addition of a bibliography, the selection and arrangement being that imposed by the text. The antiquity of most of the 350 references suggests why this book is not conspicuously more modern than the third (1901) edition of Ewing's classic work on a portion of the subject. The paper, printing and binding are adequate. For reasons already stated the book will find little favor with specialists. The American technologist may use it cautiously for numerical data, but can find elsewhere better specifications for magnetic testing than those standard in Germany in 1910. The general reader will derive from it but a confused idea of the present state of knowledge regarding magnetism. Pp. VII+306, 167 diagrams. E. P. Dutton and Co., New York, 1926. $6.00.

L. W. McKeehan

Popular Research Narratives. Vol. 2. Collected by the Engineering Foundation.—Here is a group of fifty scientific essays evidently addressed to the lay reader. The language is non-technical; the subject matter very concrete; the discoveries important; the inventions valuable. It is a collection of wonderful stories—each told within the space of three small pages. The reader is therefore not carried very far; but the growing interdependence of engineering and pure science is made very evident. Much of the pleasure of reading a book is lost when, as in the present case, one does not know who is responsible for the words; the ideas may be ever so good; one wants to know who clothed the ideas with these words. It is unfortunate also that no definite references to literature are given, such as would permit an interested reader to pursue the subject farther. But it is hardly fair to appraise these expositions from a scientific view point, as is usually done in this journal. Most students of physics will be stimulated by the account of *Permalloy, The High Temperature Electric Furnace, The Sonic Depth Finder, Talking Across the Ocean, The Geophone, Modernizing the Steam Locomotive*, and many others.

The purpose which underlies this little volume has been clearly set forth, in the introduction, by Professor Pupin who says: "Take care of the bee and the honey; enrich the field of human experience. Scientific and engineering research is the honey gathering process; men trained and disciplined in this field of inquiry are the honey gathering bees. Research and the men conducting it contribute to the honey-hearted hive of our national life. We must cultivate both, otherwise the hive will soon be empty." Most men at some period in their lives—generally an early one—have cultivated the honey bee; but the enthusiasm of the youthful apiarist is generally short-lived. The reason for this is that most bees behave as if they were perfectly familiar with Virgil's verses: *Sic vos, non vobis, etc.* At any rate, they insist upon making honey in their own way; simply because it is the greatest fun in the world, the best sport imaginable. Whether the process can be greatly expedited by the men who collect the honey may be fairly doubted. Investigators, if caught young, may be shifted from university laboratories to those of the large corporations, but whether humankind thus derives more benefit than it would from the labors of these same men in perfectly free academic laboratories is another large question. In any event, it is to be hoped this volume will help to remove that illogical distinction between pure and applied science, between what Norman Campbell calls "the roots and branches of the tree of experimental knowledge." viii+174 pp., Williams & Wilkins Company, Baltimore, 1926. $1.00. HENRY CREW

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE MONTREAL MEETING, FEBRUARY 26-27, 1926

JOINT MEETING WITH THE OPTICAL SOCIETY OF AMERICA

The 137th regular meeting of the American Physical Society was held in the Macdonald Physics Building of McGill University, Montreal, on Friday and Saturday, February 26 and 27, as a joint meeting with the Optical Society of America. The presiding officers were Dayton C. Miller, President of the American Physical Society, and W. E. Forsythe, President of the Optical Society of America. The attendance was about 100 persons.

On Friday morning there was a session of the Optical Society and a session of the Physical Society. The program on Friday afternoon consisted of papers contributed by the American Physical Society, and a lecture by Professor Frank Allen of the University of Manitoba, on "The Second Half of Vision," given by invitation of the Optical Society. The Saturday morning session was a regular session of the American Physical Society.

On Friday evening the members of the American Physical Society and of the Optical Society of America were guests of the Chancellor, the Principal and the Board of Governors of McGill University at a dinner held at the Mount Royal Hotel.

At the regular meeting of the Council held on Friday, February 26, 1926, one new fellow was elected, one member was transferred to fellowship, and fourteen were elected to membership. *Elected to Fellowship:* Abraham Joffé. *Transferred from Membership to Fellowship:* Frank M. Walters, Jr. *Elected to Membership:* John B. Bishop, Donald C. A. Butts, Herbert R. Childs, Frederick W. Cunningham, Frederick W. Doermann, Frederick H. Drake, Peter Fireman, Sydney B. Ingram, Hermann E. Krefft, Horace H. Lagerpusch, Theodore J. Martin, W. C. Phebus, Eugene W. Skinner, and Leo John Vollmayer.

The titles and abstracts of papers presented to the Optical Society of America will be found in the Proceedings of that Society, published in the *Journal of the Optical Society of America and Review of Scientific Instruments.*

The abstracts of the forty-two papers presented to the American Physical Society are given in the following pages. Papers Nos. 1, 19, 25, 33, 39, 41 and 42 were read by title. Papers Nos. 19, 33 and 35 were received after the program of the meeting had gone to press and were therefore not included in the printed program of the meeting published in Volume 1, Number 7, of the Bulletin of the American Physical Society. An **Author Index** will be found at the end.

HAROLD W. WEBB,
Secretary

ABSTRACTS OF PAPERS

1. **Diffraction by a grating.** G. BREIT, Carnegie Institution of Washington.—Frauenhofer diffraction phenomena have been explained by Duane in terms of transfer of momentum to the diffracting apparatus. It has been shown by Ehrenfest and Epstein using Compton's modification of Duane's theory, as well as by the writer on a different basis, that Duane's explanation may be made quantitative. In the present paper the requirement of proper maintenance of equilibrium in black body radiation is applied. It is shown that Duane's grating does not acquire the proper kinetic energy when exposed to black body radiation if quanta are conceived of as mechanical entities. On the contrary it is necessary to introduce probabilities of interaction similar to those used by Einstein in his 1917 needle quanta paper. In such a way the scattering by a grating is similar to the scattering by free electrons (Pauli) and by Bohr atoms. The conditions for interference come out, therefore, simply as selection rules. This point of view explains also Fresnel diffraction phenomena. This continuous transition from a Bohr atom *via* Hertzian oscillator to a grating is traced.

2. **Investigation of x-ray spectra by the method of visibility.** LACHLAN GILCHRIST, University of Toronto.—Formulæ are derived which represent the distribution of intensity and the visibility in x-ray spectra when the analysing crystal is composed of a large number of parallel reflecting planes. In the development the primary sets of multiple reflections are taken into account and the source is not supposed to be strictly monochromatic, but to have a "width." For a perfect crystal the expression for intensity is $I=[b^2(1-b^2A^6B^4)^2/(1-A^4B^4)][P+2A^2B^2C_1\cos 4\pi Dm+2A^4B^4C_2\cos 8\pi Dm+\cdot\cdot\cdot\cdot\cdot]$ and the expression for visibility is $V=A^2B^2C_1/P$, where b and a are the coefficients of reflection and absorption, respectively. $A=1-a$ and $B=1-b$. P_1C_1, C_2, etc., $2D$, and m have the significance given to them by Michelson and Rayleigh in articles on interference phenomena. This agrees with the visibility in the spectra obtained with Calcite crystals by Bergen Davis and Stempel. For crystals with random or "irregular" spacing maximum and minimum intensities are given by $I=[b^2\Sigma_0^p A^{4p}B^{4p}/(1-b^4A^4)][P\pm 2b^2A^2C_1]$ and the visibility is given by $V=2b^2A^2C_1/P$. If the intensity at the minimum is zero when perfect crystals are used, which seems to be in accord with experimental results, then in spectra which are obtained by means of imperfect crystals the intensity at the minimum is not always negligible and deductions should not be made from the intensity of the maximum alone.

3. **The fine structure of the K x-ray absorption edge of calcium.** GEO. A. LINDSAY and GEO. D. VAN DYKE, University of Michigan.—The absorption spectrum of calcium was photographed by the use of a Siegbahn vacuum spectrometer. The absorption

occurred in the calcite crystal, thus rendering a screen unnecessary. A gypsum crystal was also used. The edge obtained from the calcite crystal showed two white lines and a wider absorption region farther towards shorter wave-lengths. The gypsum showed one strong narrow white line with faint traces of a second, while the third wider absorption region was about like that from the calcite crystal. The difference between the first and the second white lines was about 13 volts, between the first edge and the beginning of the third, about 30 volts. If the calcium is in the form of an ion in the compound, the K electron which is removed by the absorption is more likely to stop in one of the orbits normally occupied by the valence electrons, or in an orbit somewhat farther out than it would be if the atom were neutral, for the ion has a net charge of +2. This may explain the appearance of the white lines. These multiple edges seem to be found oftener for compounds (which are probably ionized) than for elements.

4. The scattering of x-rays. J. A. GRAY, Queen's University.—The x-rays scattered from different thicknesses of material have been examined by an absorption method. The thinner the material, the greater is the average wave-length of the issuing radiation. The results indicate that the modified "band" in scattered x-rays has a greater total intensity than is commonly supposed. From these and other results, it seems possible to explain the small intensity of reflection of x-rays from crystals for the larger angles of scattering. No evidence for the J phenomena has been found.

5. Cross-sectional area of an Einstein quantum. R. J. PIERSOL, Westinghouse Research Laboratory.—A gas kinetic treatment of the equilibrium of light quanta and electrons led Burger and Ornstein to the value $\alpha\lambda^2$ for the cross section of a light quantum, where α is a universal, but unknown constant. By calculation from the vibration volume of the electron Marx showed $\alpha=3/4\pi$, or that the area $A=3\lambda^2/4\pi$. It may be proved from the classical Hertzian theory of oscillators that, if the two electric doublets are parallel, the area of thermal absorption $A_t=3\lambda^2/4\pi$, which is identical with the result obtained by Marx from equilibrium considerations. But it is shown, in general, that where there are a large number of radiating and absorbing electrons, oriented at random, the area of electromagnetic absorption is $A_e=\lambda^2/\pi$. Therefore, the unknown constant in the equation of Burger and Ornstein is $\alpha=1/\pi$ instead of $\alpha=3/4\pi$. Numerically this value is very close to that obtained by Marx, and therefore either value satisfies the interference and diffraction of light.

6. Radiation arising from the formation of helium from hydrogen. G. E. M. JAUNCEY and A. L. HUGHES, Washington University.—The loss of mass when four protons and two electrons come together to form a helium nucleus signifies a loss of energy which appears as a quantum. Conservation of energy and of momentum must both be satisfied. Four processes are considered: (1) the protons and electrons initially at rest produce a helium nucleus recoiling in the opposite direction of the quantum, (2) the protons and electrons all initially having velocity βc produce a helium nucleus at rest, (3) one proton with velocity βc meeting three protons and two electrons at rest produces a helium nucleus at rest, (4) one electron with velocity βc meeting four protons and one electron at rest produces a helium nucleus at rest. Solving for λ and β we find: $\lambda=.0004$A in (1), (2), (3) and .0008A in (4); $\beta=.008$ in (1), (2), .03 in (3) and .9995 in (4). The reverse of (4) is the photo-electric effect. By analogy with x-rays, .0004A and .0008A may be considered as critical absorption wave-lengths. This suggests looking for a trace of hydrogen in a tube of helium after the tube has been exposed to the penetrating rays studied by Millikan.

7. Radiation from the mutual annihilation of protons and electrons. A. L. HUGHES and G. E. M. JAUNCEY, Washington University.—Mutual annihilation of a proton and an electron on collision giving a quantum of radiation of wave-length 1.3×10^{-5} A has been suggested as the source of the high frequency radiation studied by Millikan.

It can be shown that this simple process cannot simultaneously conserve energy and momentum. Moreover it is difficult to imagine the reverse process, which would require a quantum suddenly, without apparent cause, to disappear, leaving in its place a proton and an electron. Both energy and momentum can be conserved in a *three body* collision. *Two electrons and one proton* colliding result in a recoil electron moving with a minimum velocity .9999995*c*, and a quantum whose wave-length is 2.6×10^{-5}A (or less). *Two protons and one electron* colliding result in a recoil proton moving with a minimum velocity .6*c*, and a quantum whose wave-length is 1.9×10^{-5}A (or less). The reverse process is as easy to realize as the forward process. An electron (or a proton) colliding with a quantum (having sufficient energy) causes the quantum to disappear leaving two electrons and one proton (or two protons and one electron).

8. The "reflection" of electrons from the molybdenum target of a Coolidge x-ray tube. W. R. Ham and Marsh W. White, Pennsylvania State College.—The method previously described by the writers (*Phys. Rev.* **27,** 111, (1925)) was used. This consists essentially of accurately measuring the energy input into the tube and the heat energy received at the anode. An approximate measure of the ratio of the number of impinging electrons to those emitted from the anode is obtained by taking the ratio of (W_i-W_a) to W_i, where W_i is the energy input and W_a is the heat energy received by the anode alone. In the present experiments the data have been extended, with improved technique, to include molybdenum. The tube used was a standard molybdenum-button water-cooled type. Several improvements in the experimental arrangements were made, namely: the temperatures of the water used in the flow calorimeter were read to 0.001 degree by Beckmann thermometers, the water supply was changed to an elevated constant temperature bath and arrangements were provided for keeping the room temperature constant. The curve showing the percentage of "reflected" electrons vs. voltage is similar to that for tungsten, rising from 20 to 1.3 kv to a pronounced maximum of 22.5 at 4 kv and rapidly falling off to 3 at 20 kv, where it remains approximately constant up to 30 kv.

9. Reflection of soft x-rays. Elizabeth R. Laird, Mount Holyoke College.—This work continues some done in 1922 with a thermoluminescent detector. Electrons from a low temperature cathode fall on a target, the x-radiation produced passes through a tubular slit into a reflector which can be set at different angles or pulled aside. The reflected or incident beam falls on a Schumann plate. For copper at 1000 volts the result indicates total reflection at a glancing angle of about 5°, and very little for larger angles. At 500 volts the transition is less marked. For this voltage strong reflection occurs at 25°, for 265 volts at 35°, and for 160 volts at 8°. For larger angles the reflection at 160 volts is not as strong as at 265 volts, suggesting the passing of a natural frequency. Nickel at 500 and 1000 volts is similar to copper. Aluminum at 265 volts shows little reflection. Computation of critical angles by the Drude-Lorenz formula depends on values ascribed to natural frequencies, and to wave-lengths of maximum energy for a given voltage. Values for copper of 4° and 14° were computed for 1000 and 500 volts. The experiments show that these Schumann plates become less sentisive for equal energy as wave-length diminishes. The experiments will be continued looking towards more precision in measurement. This work was done at the Sloane Laboratory, Yale University.

10. Electron distribution in sodium chloride. Arthur H. Compton, University of Chicago.—Extending Duane's method of Fourier analysis, a series expression is obtained for the mean electron density at different distances from the centers of the atoms in a crystal. Every term in the series may be determined by measurements of the intensities of the reflection of x-rays from the crystal, whereas in Duane's method a constant term remains undetermined. Using the data of Bragg, James and Bosanquet for the reflection from rock-salt, the electron density is found to fall definitely to zero for the sodium ion 1.1A, and for chlorine at 2.0A. from the center. Sodium has a group of eight electrons (probably K and $L2_2$) near the center with two electrons (probably $L2_1$) at .9A from the center. Near the center of the chlorine ion are 10 electrons (K and L) outside of which are eight others, resolvable into $4(3_3?)$ at .74A, $2(3_2?)$ at 1.14A and $2(3_1?)$ at 1.60A. These distances are uncorrected for thermal agitation. The electron distribution curves are similar to but show more detail than those obtained by Bragg and Havighurst from the same data.

11. Crystal size and hysteresis in precipitated magnetite. LARS A. WELO and OSKAR BAUDISCH. The Rockefeller Institute for Medical Research.—Magnetite has been prepared by three methods previously described (*J. Biol. Chem.* **65**, 216, (1925)). These oxides will be referred to as Lefort's, Haber's, and B and W's. In the present study the usual method of preparation of the latter oxide was departed from by boiling in excess of alkali. The oxides are of identical crystal structure but the average crystals differ in size. This is known from the relative sharpness and diffuseness of the diffraction lines. Lefort's oxide has a small average crystal, Haber's an intermediate size, and B and W's the largest crystals. Their magnetic properties have been studied. Barring the unknown but possible influence of impurities (sulphates to the extent of about 2 per cent) unavoidably occluded at the moment of precipitation, the conclusion is that lean hysteresis loops, low coercivities and low remanences are associated with oxides composed of small crystals. The significant constants for Lefort's, Haber's, and B and W's oxides are respectively: permeability maximum at 50, 240 and 380 gausses; coercivity of 14, 67 and 149 gausses; remanence of 8, 18 and 34 per cent. The relative areas of the hysteresis loops are as 1, 5 and 7.

12. A method for exciting spectra of certain metals. JOHN K. ROBERTSON, Queen's University.—An examination of the spectrum of tin when excited by the electrodeless discharge has shown that characteristic metal lines are brought out in the case of a discharge in a quartz tube containing residual gas and pieces of cold metal to about the same extent as when the tube was heated to 1000°C. To study the origin of the metallic lines, other metals were examined, in all cases sufficient hydrogen being left in the quartz tubes to carry the discharge. With silver and gold negative results were obtained, but with zinc and cadmium lines were present as in tin. Moreover, with these two metals, only ultimate and penultimate lines of the neutral or the ionized atom appeared. In cadmium, for example, the quartz spectrograph showed with marked intensity only $2144(1\sigma-1\pi_1)$, $2265(1\sigma-1\pi_2)$, $2288(1S-1P)$, $3261(1S-1p_2)$. Evidence is given that the explanation of the effect is found, not in the presence of vapor due to temperature, but as a result of some kind of reaction between active gas atoms and the metal or an oxide of the metal. The appearance of ultimate ionized lines and the non-appearance of higher members of neutral series is, however, somewhat puzzling.

13. Spectrum of copper. A. G. SHENSTONE, Princeton University.—In addition to a normal doublet spectrum, the copper arc yields a complicated spectrum built on the low inverted ^2D term which connects the two spectra. The Heisenberg-Hund theory predicts low terms ^4P, ^4D, ^4F, ^2P, ^2D, ^2F which should combine with the ^2D. Zeeman effects obtained on a Hilger E.1 spectrograph identify the term $\nu=22194.0$ as $^4P_2$ and $\nu=21364.3$ as $^4P_1$. The latter has a g equal to $2.5\pm.1$, (theoretical value $=8/3$). The two terms $\nu=17392.3$ and $\nu=16487.2$ have irregular g values equal to $.21\pm.01$ and $.51\pm.02$. They may be $^4D_1$ and $^2P_1$. The term $\nu=17763.9$ has $g=1.1\pm.1$ which must also be irregular. All the evidence indicates that this portion of the Cu spectrum has the characteristics of a spectrum of the second rank. In all 20 positive terms combining with ^2D have been found. These in turn combine with 21 negative terms and account for 175 arc lines including all the important ultra-violet and most of the important visible lines. Some constant frequency differences have been found connecting the prominent ultra-violet Cu^+ lines. Several lines have been identified from Zeeman patterns.

14. Standard wave-lengths for use in the extreme ultra-violet. STANLEY SMITH and R. J. LANG, (introduced by R. W. Boyle). University of Alberta.—Wave-lengths of a number of lines, chiefly of carbon, which frequently occur in the spectra of other elements, have been measured in the second and third orders on plates obtained in a vacuum spectrograph with a concave grating of radius 6 feet ruled with 30,000 lines to the inch. The dispersion was approximately 4.5A per mm. The carbon lines and the iron standard lines used as comparisons were obtained *simultaneously* by passing a condensed spark discharge between a carbon and an iron electrode. (1) *Method of measuring.* Details are given of a new method of obtaining the curves to correct (a) for deviation of the spectra from normality (b) for error in the tilt of the photographic plate. These curves can be used for correcting the calculated wave-lengths obtained by interpolation between any pair of standards chosen within the range of the curves. The curves for correction (b) are proved to be very approximately parabolic. (2) *Wave-length measurements* of the following lines have been made: 904, 977, 1010, 1036, 1175, 1215, 1247, 1323, 1329, 1335, 1548, 1550, 1561A.

15. Stark Patterns. J. STUART FOSTER, H. B. HACHEY and W. ROWLES, McGill University.—The simplest Stark pattern consisting of one parallel component and no perpendicular component (1/0) is observed for three members of the orthohelium series $2s-ms$. This pattern, together with others previously reported by one of the writers (Nature **116,** 135 (1925)) completes a group of Stark patterns 1/0, 1/1, 2/2, 2/3 which theoretically exist in the Balmer series. The parhelium combination line $2P-6P$, next the diffuse line in the 4144 group, is clearly observed as a separate line in lowest field. The dispersion 3A/mm makes the separation (0.26A) of these lines more definite than in a previous experiment (Phys. Rev. **23,** 667, 1924). The orthohelium lines near and including 4026 are observed as doublets in high electric fields. The observed separation is constant throughout.

16. A method of measuring relative intensities of Stark-effect components. J. STUART FOSTER and M. LAURA CHALK, McGill University.—A modified Lo Surdo tube with rectangular cross-section near the cathode is employed. At a given distance from the cathode the light intensity is constant over the central portion of the discharge in the Crookes dark space. The tube is placed with its axis horizontal and with the longer side of the rectangle in a vertical position. Light from very near the cathode is analyzed and found to give straight lines of uniform intensity corresponding to the different Stark-effect components. Using this source and a double neutral wedge, photographs of the p and s components of $H\beta$ are obtained from which the relative intensities are measured. Final results will be published when a check has been made on the wedge calibration.

17. Interpretation of complex spectra. OTTO LAPORTE, Research Fellow, Bureau of Standards.—Recent development of the theory of atoms with several valence electrons, permits interpretation of the complex arc and spark spectra of the two long periods of elements. The low and metastable term group of the spectrum of an element with z valence electrons and belonging to the second long period can be accounted for by the three configurations: $(z-2)$ electrons of type 4_3 and two 5_1, $(z-1)$ of 4_3 and one 5_1, z electrons of 4_3 and none of type 5_1. Hund has shown that the first and second kinds represent respectively the normal states of the neutral and simply ionized atoms from Ca to Ni. In the second long period, it is possible to show the presence also of terms belonging to the third configuration in almost every spark spectrum. The tendency to eliminate the 5_1 electrons gradually becomes stronger towards the end of the period:

Neutral Pd and the singly ionized atoms from Cb to Ag are normally in states with 4_3 electrons only. The new theory connects term differences in the spark with differences of series limits in the arc spectra. This is illustrated with Cr and Fe.

18. Approximating the "screening constant." D. T. Wilber, Cornell University.—A combination is proposed of the Sommerfeldt assignment of azimuthal quantum numbers of 1, 2, 3, 4, to the s, p, d, and f, terms, respectively and his value of the term energy, $R(Z-s)^2/n^2$ plus a negligible term, with a proposed approximation value for the "screening constant" s. This value takes the form $s=(1-1/(4n)^k)(Z-1)$ and $\nu=R[(1+(Z-1)/(4n)^k)^2/n^2]$ is the energy value of a term of total quantum number n and azimuthal quantum number k. Calculating the value of the series terms of the alkalies from this formula gives a good check for the four series of lithium and follows the trend of the sharp terms up to caesium but shows a systematic and finally large deviation in the case of the p terms. In general this systematic deviation is proportional to the doublet separation. This formula does not compete with the Rydberg, Ritz or Hicks formulæ for accurate interpolation but does show how Bohr's values of total quantum number can be possible when so much larger than the usual value assigned the terms.

19. Electronic states of molecules and structure of band spectra. Robert S. Mulliken, Harvard University.—Postulates: (1) The electronic states of molecules can be characterized by term designations (^1S, $^2p_1$, etc.), each associated with an electronic quantum number j_e substantially identical with *Sommerfeld's* atomic j for the given term-type, and representing the *true* resultant electronic angular momentum of the molecule (or in some cases *each atom* may have its own j_e). (2) The vector or vectors j_e set themselves essentially parallel ($\pm\epsilon$ components) or perpendicular (σ components) to the vector m representing the nuclear precessional quantum number; the nuclear rotational energy is then given by a Kratzer-Kramers and Pauli formula $F(m)=B((j^2-\sigma^2)^{\frac{1}{2}}\mp\epsilon)^2\ldots.$; $j=$final resultant of m, ϵ, σ. (3) j has integral values for odd molecules, half-integral values for even molecules, and is subject to the selection principle $\Delta j=0, \pm 1$, the transition $\Delta j=0$ (Q branches) being always present except when $\sigma=0$ for both initial and final states, as predicted by the correspondence principle. These postulates, which are the outgrowth of work of Kratzer, Birge, Mecke, and others, appear capable of accounting in a unified way for many of the features of the structure of most known band spectra, and promise important information on molecular structure, orientations and other characteristics of molecular and *atomic* electron orbits, etc.

20. Critical potentials and the heat of dissociation of hydrogen as determined from its ultra-violet band spectrum. Enos E. Witmer, National Research Fellow, Harvard University.—Lyman has found that under certain conditions of excitation the mixture of hydrogen with argon causes the former to emit a very simple, one-dimensional series of bands, lying between λλ 1063 and 1670. These bands are apparently Q branches with perturbations near the origin, and, as this investigation indicates, are excited as follows. The energy imparted to a hydrogen molecule is limited to 11.6 volts, the resonance potential of argon. This is just sufficient to raise the hydrogen molecule from the normal state, $e_t=1$, $n=0$ to $e_t=2$, $n=0$, where e_t is the total electronic quantum number, and n the vibrational. Returning, the jumps are $e_t'=2$, $n'=0$, to $e_t''=1$, $n''=0$ to 12. The curve (n'', dE/dn'') indicates that dE/dn'' becomes zero shortly beyond $n''=12$, so that at $n''=12$ the molecule is on the verge of dissociation, and $n''=13$ apparently cannot exist. The data give the following molecular constants: lowest resonance potential = 11.61 volts; the heat of dissociation = 4.27 volts = 98,570 calories in agreement with Isnardi's (Zeit. Elektrochemie **21,** 405, 1915) value of 95,000 calories; the frequency of infinitesimal vibration ω_0 in the normal state = 4260 cm^{-1} in fair agreement with the value 4880 cm^{-1}, obtained by Kemble and Van Vleck (Phys. Rev. **21,** 653, 1923) from specific heat data. Combining this resonance potential with other spectroscopic data gives 15.2 volts as the probable ionization potential of H_2.

21. **Flow of ions through a small orifice in a charged plate.** L. Tonks, H. M. Mott-Smith, Jr., and I. Langmuir, General Electric Co.—To separate the ionic and electronic parts of the electric current to an electrode immersed in an arc, A. F. Dittmer suggested allowing the carriers to pass through small holes in one electrode, B, and collecting them on a second close parallel electrode, C. The undesired carrier can be prevented from reaching C by the potential of either B or C. Practically B must be negative with respect to sheath-edge A, C positive with respect to B. We have calculated the electric field about a circular hole in a thin infinite charged plate, the transverse velocity acquired by a fast charged particle passing through the hole and the effective change in the area of the hole due to focusing action. These results enabled us to calculate the volt-ampere characteristic of C when collecting electrons having a Maxwellian distribution, or ions having Maxwellian and quasi-Maxwellian velocity distributions. The usual semi-log plot of the electron characteristic yields a temperature which is slightly high, the ion characteristic is linear for small accelerating voltages and its semi-log plot for retarding voltages is curved. The determination of current densities and carrier temperatures from the characteristics and the errors involved have been worked out.

22. **Positive ray analysis of the ions in a discharge in hydrogen.** H. D. Smyth and C. J. Brasefield, Princeton University.—Previous experiments by one of the authors and others indicate the importance of H_3^+ as a product of ionization in hydrogen. Considering the possible bearing of this result on the interpretation of the many lines spectrum the authors are now studying the relative concentrations of different types of ion in a striated discharge. The discharge is maintained between a filament and plate 20 cm apart in a tube of 5 cm diameter. In the side of the tube about half way between plate and filament is a third electrode, to which positive ions are drawn. Through a slit in this electrode some of the ions pass into a positive ray analysis apparatus of the type used before. Preliminary results give sharply defined "peaks" which are identified as due to H_3^+, H_2^+, and H^+. When the ions are drawn from the positive column, the H_3^+ ions are by far the most numerous though the H^+ peak is also strong. The H_2^+ peak is very weak increasing only slightly when the pressure is reduced from .2 mm to .03 mm. However at a pressure of .005 mm H_2^+ becomes slightly stronger than H_3^+. Experiments are being continued.

23. **Analysis of positive ions emitted by a new source.** G. P. Harnwell, Princeton University, and H. A. Barton, Harvard University.—Certain iron oxide crystals containing about 1 per cent of some alkali metal or alkaline earth have been developed by the fixed Nitrogen Research Laboratory for use as catalysts in the synthesis of ammonia. It has been found that these substances have also great utility as constant and abundant thermionic emitters of positive ions (Kunsman, *Science*, **62**, 269 (1925)). The writers have analyzed their emission by the use of a mass spectrograph which has been described by Smyth. Separate catalyst samples containing respectively Na, K, Rb, Cs, Mg, Ca, and in one case both Ba and Sr have been shown in this way to emit only the corresponding singly charged positive ion. No doubly charged ions were observed, nor any ions of the other elements composing the catalysts. The alkali metal ions were emitted at lower temperatures than the alkaline earth ions. Particularly in the case of the latter, a preliminary treatment consisting of reduction at red heat in an atmosphere of hydrogen increased the emission.

24. **The passage of charged particles through helium.** A. J. Dempster, University of Chicago.—The penetration of protons with 300 to 900 volt velocity in helium, reported in a previous paper, has been found to hold for much slower rays. With 14 volt rays the charged bundle of rays was observed at a helium pressure that would give six collisions for the path completed. The average loss of velocity per collision for the

majority of the rays of 900 volt speed in penetrating 15 to 25 helium atoms is less than half a volt per collision. Other ions are neutralized or dissociated in helium, and an approximate free path may be deduced from the rate at which they disappear as the pressure is increased. With hydrogen molecule ions the free path for dissociation of 900 volt rays is about 17 times the kinetic theory mean free path for helium atoms. With slower rays (340 volts) the free path is still larger, 2.5 times greater than for the faster rays. Singly charged helium atoms are rapidly neutralized. If we calculate the number of collisions assuming an ion diameter equal to the atomic diameter given by the kinetic theory of gases, the helium ion makes, on the average, only 2.8 collisions before neutralization.

25. Report on the failure of the mercury to gold transmutation experiment. H. HORTON SHELDON and ROGER S. ESTEY, New York University.—During the past year we have repeated the mercury to gold transmutation experiments of Dr. Miethe of Berlin and we have not been able to produce the slightest trace of transmuted gold. Our runs were made in three lamps; one horizontal, one vertical, and one a copy of that used by Miethe. The first ran for 30 hours, the second for 50 hours, and the third for 172 hours. The mercury from each run was carefully analyzed and the analyses checked with blank tests of minute known amounts of gold. We found no transmuted gold whatever, although a quantity fifty times smaller than Miethe claims to have produced in 197 hours was detectable with certainty. It is claimed that transmutation is due to instability of the arc conditions. Our experiments seemed to show more instability than that reported by Miethe, thus refuting that suggestion. The suggested explanation of a change of the number of electrons in the nucleus changing mercury to gold seems good in theory, but incredible in fact, for the potential drop per mean free path of a mercury molecule is only about 0.1 volt in these arcs.

26. A method of high precision for the determination of critical potentials and the ionization potential of mercury vapor. ERNEST O. LAWRENCE, National Research Fellow, Yale University.—Electrons from a hot cathode are bent into circles by the magnetic field of 60 cm Helmholtz coils, a portion thereof passing through a series of slits on a circle of 5 cm radius. Using a positive ion sheath to neutralize space charge, currents of the order of 10^{-9} amp. for ten-volt electrons emerge from the final slit. Retarding potential measurements show that the electrons have a sharp upper limit to their velocities which is the condition necessary for sharp critical potential curve "breaks" and ultimate precision in critical potential measurements. Such a beam of electrons was passed into the effectively field free space of a Faraday cylinder containing mercury vapor and a suitable electrode arrangement for detecting the formation of positive ions. Observing the potential of the cylinder at which ionization is detectable and the potential requisite to prevent the entrance of electrons gave the value 10.4 volts as the ionization potential of mercury vapor with a possible error of about one-half of one per cent. The method is so precise that the errors no longer lay in corrections for the curve breaks but in the measuring instruments.

27. Ionization potential and radius of the atom. A. S. EVE, McGill University.—The ionization potential is roughly inversely proportional to the radius of the atom as already shown for Group I and II in the periodic table (Nature **107,** 552 (1921)). This relation holds well for the rare gases whether the kinetic theory or Bragg's x-ray radii are selected. Glockler (*Phil. Mag.*, **50,** 997 (1925)) has directed attention to this relation, which is investigated more closely in the present communication.

28. Photo-ionization of a gas by a discharge in the same gas. F. L. MOHLER, Bureau of Standards.—Measurements were made in a tube containing two thermionic units electrically screened from each other; one serving to give a discharge at measured current and voltage, the other operated at a constant low voltage so that the electron emission was limited by space charge. Photo-ionization of the gas in the second unit was detected by the increased thermionic current, resulting from neutralization of the space charge. Relatively little photo-ionization is produced by the arc spectrum while a strong effect is produced when the discharge voltage is sufficient to produce higher stages of excitation. The method is therefore well adapted for measuring higher critical potentials. Some of the results obtained are as follows: Caesium; ionization of 6_2 shell 13.0 volts, double ionization 21.5, ionization of 6_1, 39.0—Potassium; double ionization 32, ionization of 3_1 shell 48—Argon; double ionization 34.8, ionization of 3_1 shell 39.6—Neon; double ionization 54.9. In each case the most pronounced increase in photo-ionization came at the double ionization point and spark excitation stages at slightly lower voltages were also found.

29. Reconciliation of experiments on probability of ionization by electron impact. K. T. Compton and C. C. Van Voorhis, Princeton University.—Recent work in this field by Hughes and Klein, Jesse and the authors, shows considerable lack of agreement. It is shown that that of Hughes and Klein and of the authors is brought into fair agreement by correcting for three sources of error: (1) effect of the electric field on the effective area of holes in the grid through which primary electrons pass; (2) presence of slow secondary electrons and lack of homogeneity in velocities of primary electrons; (3) warming of gas by filament. These three corrections were determined for an apparatus built like Hughes and Klein's. The second one only applies to our earlier results. As a result of such corrections our earlier values should be increased by about 10 per cent at electron velocities above 100 volts and somewhat more at lower velocities, and Hughes and Klein's results and ours are brought into approximate agreement. We could not reconcile Jesse's results with the others. Final corrected values of probability are given.

30. Small Einthoven galvanometer. Horatio B. Williams, Columbia University.—Theoretical work undertaken for another purpose pointed to the possibility of designing a very small string galvanometer. Criticism of the theory and comparison of its consequences with experimental data having shown its probable soundness, the instrument was designed and built. Its performance corresponds with predetermination. It weighs 5.2 kg which may be compared with 100 kg, the weight of the original instrument, and 18 kg, the weight of the smallest accurate and sensitive string galvanometer hitherto available. The stray field has been much reduced, and at a short distance from the instrument is of the same order as that from an ordinary ammeter with permanent magnets at the same distance. The powerful optical system of the larger instruments is retained. Strings are mounted in interchangeable carriers. The instrument is robust and portable and at ordinary sensitivities very little affected by mechanical vibration. A sensitivity of 5×10^{-10} ampere/cm has been easily attained and is probably not the limit of its performance.

31. A precision determination of the electrical conductivity of concentrated aqueous solutions of calcium chloride. Marguerite Crow, McGill University. (Introduced by A. Norman Shaw).—Measurements are reported which give the electrical conductivity of solutions of calcium chloride for concentrations of from 25 percent to 50 percent and for temperatures from 10°C to 30°C with an increased precision of 5 parts in 10,000. The following are sample readings near the upper and lower limits of that part of the range over which accurate measurements are new:

Temperature	Concentration by weight	Specific conductivity
16.50°C	46%	.05482
11.02	38.35	.09314
26.10	46	.07349
26.43	38.35	.13695

The determinations of temperature coefficients are given for a more extended range than heretofore; for example, at 18°C, the temperature coefficient at 45% is .0320, whereas at 20%, it is .0197. Variations of this coefficient are tabulated. The method consisted of an application of the standard Washburn method for precision conductivity measurements including auxiliary calibrations and the development of a simple technique for obtaining densities of deliquescent solutions and for transferring them to the conductivity cell, without the opportunity for evaporation. These data were required in connection with the determination of vapor pressure by the measurement of electrical conductivity of thin films of solutions as used in an electrical hygrometer; but the results appear to be of independent value for extending existing tables of conductivity.

32. **The redetermination of the temperature coefficients and the ageing corrections for new and old standard cells of the normal and the acid types.** H. E. Reilley and A. Norman Shaw, McGill University.—The use of "ageing" corrections has made it possible to determine the relative "international mean" for the electromotive force of a normal standard Weston cell from the measurements of a few old cells with a degree of accuracy equal to that obtained by using large numbers of new cells, actually within six microvolts. This has been checked by ten formal exchanges of cells with the Bureau of Standards and the National Physical Laboratory, Teddington, over a period of seventeen years, giving close agreements of high precision. The following sample figures indicate the variation in the ageing for a particular batch of five normal cells, of which the average deviation from their own mean did not vary more than three microvolts in seventeen years: *Ageing correction in microvolts for normal cells made in 1908*; 1909, +6; 1912, +28; 1919, +54; 1926, +68. The temperature coefficients of old normal cells remain unchanged, while those of acid cells more than two years old appear to be relatively erratic. Rules for procedure in analyzing the data of cell comparisons have been reformulated.

33. **Relativity and radiation.** A. S. Eve, McGill University.—Equate the relativity expression for mass to the corresponding quantum value, and we have for the *complete* disappearance of mass m, $h\nu = mc^2$. But $\nu = c/\lambda$, so that $\lambda = h/mc$ (Home). Now give m (1) the mass of an electron, (2) the mass of a hydrogen atom, (3) the change of mass when 4 H atoms form one He atom; viz., $m = 1/1800$, or $= 1$, or $= .032$ times 1.66×10^{-24}. Then the corresponding values of λ are 2.3×10^{-10}, 1.3×10^{-13} (Jeans), 4×10^{-11} (Millikan); and of T are 4×10^{19}, 7×10^{12} (Jeans), 2×10^{11} degrees absolute, if we put $h\nu = mc^2 = (3/2)\, k\, T$. Dr. King prefers $\lambda_{max} T = c = 1.447$, so that if $\lambda_{max} = 1.3 \times 10^{-13}$, $T = 11 \times 10^{12}$, not far from the 7.5×10^{12} which Jeans suggests.

34. **The Hall effect in sodium and potassium.** E. S. Bieler, McGill University.—It is not generally recognized that there is one group of metals for which the Hall effect is strictly normal, as far as present measurements indicate, namely the metals of Group I of the periodic table. Data for Cu, Ag, and Au are fairly numerous and concordant; those for the alkali metals are scanty. Tests have been carried out on samples of Na and K filtered in a vacuum when in the molten state, and cast in glass cells of suitable shape. The results indicate that the Hall effect is what would be expected if these metals have one conducting electron per atom. The experiments are being carried on with Li, and will be continued with Rb and Cs.

35. **Thomas Young's Eriometer.** W. F. Emmons, McGill University, (introduced by A. S. Eve).—Adaptations of the eriometer have been evolved in two forms: (1) A large scale laboratory apparatus for projection or exact measurement. (2) A portable form with dry cells and electric bulb, giving measurements of the diameters of the spores of fungi or of blood corpuscles. The coronas of blood smears on glass slides permit diagnosis of pernicious anaemia owing to a distinct increase of diameter in such cases. The portable instrument can be calibrated by the standard laboratory instrument.

36. The electro-magnetic equations of light propagation in molecular media of varying density. Louis V. King, McGill University.—If (X, Y, Z) be the electric intensity in the incident light-wave at (x, y, z), it is customary to add to the displacement-current $(1/4\pi)\partial X/\partial t$ the convection current $ne\,dx/dt$ arising from the motions of the dispersion charge e at (x, y, z) having space-density n. The equation (1) $(u, v, w)=(1/4\pi)\partial(X, Y, Z)/\partial t+ne(\dot{x}, \dot{y}, \dot{z})$ for total current densities (u, v, w) at (x, y, z) is usually stated to follow from the *fundamental* Maxwell-Lorentz equations (2) $(u, v, w)=(1/4\pi)\partial(X, Y, Z)/\partial t+\rho(\dot{x}, \dot{y}, \dot{z})$ ρ being, however, the space-density of electricity supposed continuously (and uniformly) distributed. In fact, a closer examination requires us to replace (1) by three equations of the type (3) $u=(1/4\pi)\partial X/\partial t+ne\dot{x}+(1/4\pi)\int[(\xi-x)/r^3][\partial(ne\dot{\xi})/\partial\xi]dV$, where $r^2=(\xi-x)^2+(\eta-y)^2+(\zeta-z)^2$, the volume integral being taken to include all dispersion charges. It thus appears that (1) as derived from (2) is exact only for media of constant density and of unlimited extent. The additional term in (3) may be expected to give rise to second order phenomena such as *light scattering* arising from elastic density fluctuation due to thermal agitations.

37. Cavitation in the track of an ultrasonic beam. R. W. Boyle and G. B. Taylor, University of Alberta.—In a short paper in 1922 the first of the authors pointed out the possibility of the amount of sound wave energy transmissible through a fluid being limited by a phenomenon of cavitation, the evidence of which would be the formation of bubbles in the track of the waves. This phenomenon has been observed experimentally in the case of ultrasonic waves, where the energy is concentrated in the form of a narrow angle beam. Considering only hydrostatic pressure (p_0) as a preventive of disruption in the medium, the maximum energy transmissible across a square centimeter would be $p_0^2/2\rho c$, ρ being the density of the medium and c the velocity of the waves in it. But experiments, in a preliminary study of this phenomenon, have shown that bubbling is more readily produced in highly volatile liquids; in which case, taking vapor pressure (p_v) into account, the maximum energy transmissible per sq. cm would be $(p_0-p_v)^2/2\rho c$. The preliminary experiments show that cavitation occurs at much lower energies still, the energies being measured by the method of the torsion pendulum. It is evident that this phenomenon can limit the amount of energy transmissible in sound waves.

38. The relation between the thickness of a partition in a medium and its reflection of sound waves—by the ultrasonic method. R. W. Boyle and J. F. Lehmann, University of Alberta.—Experiments carried out by the authors a few years ago by the method of ultrasonic waves—which offer convenience in this type of work—throw light on the problem of the reflection of sound waves by serving to confirm fairly well the existing mathematical theory by Rayleigh. From this theory, which in one aspect is approximate only, it can be deduced that at perpendicular incidence there should be maximum reflection of sound energy when the thickness of the partition is one-quarter the length of the wave in its material, and there should be no reflection but perfect transmission (neglecting absorption) when the thickness is a half wave-length. In the use of a torsion pendulum to make energy measurements in ultrasonics, a means is offered to test these points experimentally. Such tests gave the best thickness of vane to be used for torsion pendulums in absolute measurements. Incidentally from the results of these tests the modulus of elasticity and the velocity of sound in the material of the pendulum can be determined.

39. Measurements of street noise in New York City. E. E. Free, 175 Fifth Ave., New York City.—A systematic survey has been made of the street noise of New York City, using the 3-A audiometer devised by the Bell Telephone Laboratories, Inc. A standard buzzer note produced by this instrument is allowed to enter the ear of the observer, simultaneously with the street noise. The intensity of the buzzer note is adjusted until it just masks the street noise. Street noise was found to be due practically entirely to traffic, the automobile truck being by far the greatest noise producer, with street cars and the Elevated Railway making much smaller contributions to the noise level. The physical intensity of the street noise, estimated by calibrating the ear of the observer, was found to vary between approximately .001 dyne per square centimeter and approximately 20 dynes per square centimeter.

40. The production and measurement of a beam of neutral molecules. Thomas H. Johnson, Yale University.—A beam of mercury vapor was formed by a condensation method similar to that used by R. W. Wood (Phil. Mag. **30**, 300 (1915). Mercury was heated to a vapor pressure of 8 cms. The vapor passed from the heating vessel through two holes 0.25 mm in diameter which were separated by a liquid air cooled chamber 8 cms long, thus permitting a sharp beam of vapor to issue from the second hole into an evacuated region beyond. An ionization gauge of the Dushman and Found type having a capacity of 20 cm was used to explore the beam. The guage was completely closed except for a slit 0.05 mm by 0.2 mm and was so mounted that the slit could be moved along a line intersecting the beam at a right angle at a distance of 8 cms above the last hole. When the slit was placed in the beam the pressure in the gauge increased from 1×10^{-5} to 3×10^{-5} mm. The half-value period for pressure changes was about 3 secs. An experiment is now in progress in which the beam is to be sent through a non-uniform magnetic field and the magnetic moment of the mercury atom measured by the deflections observed with the ionization gauge.

41. Thermal expansion of tungsten. Peter Hidnert and W. T. Sweeney, Bureau of Standards.—This paper gives the results of an investigation on the linear thermal expansion of tungsten (99.98 per cent) over various temperature ranges between −100 and +500°C. The expansion of tungsten is given by the following empirical equation: $L_t=L_0[1+(4.28t+0.00058t^2)10^{-6}]$, where L_t represents the length of the metal at any temperature t between −105 and +502°C, and L_0 the length at 0°C. Average coefficients of expansion for various temperature ranges are given in the following table.

Average Coefficients of Expansion per Degree Centigrade.

−100 to −50°C	4.2×10^{-6}	−100 to 0°C	4.2×10^{-6}
− 50 to 0	4.3;	0 to 100	4.3;
0 to +50	4.3;	0 to 200	4.4;
+ 50 to 100	4.4;	0 to 300	4.5;
100 to 200	4.5;	0 to 400	4.5;
200 to 300	4.6;	0 to 500	4.6;
300 to 400	4.7;	−100 to 500	4.5.
400 to 500	4.8;		

42. Heat transfer in the annular space between two coaxial cylinders. S. R. Parsons, University of Arkansas.—Two brass tubes are mounted with a common axis, one inside of the other, and are warmed by driving hot air, in turbulent flow, through the annular space between them. The rates of transfer of heat to the two tubes are compared by means of a coefficient representing heat transmitted per unit time per unit area of metal surface per unit difference of temperature between metal and air. Lees has shown that in streamline flow there would be a difference in the surface friction per unit area for the two tubes, and if that were true of turbulent flow, there should be a corresponding difference in the coefficients of heat transfer. Experiments show that if there is such a difference, it is not of the magnitude that would be expected from Lees' equations, and fail to show with certainty that any difference exists.

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ON THE IRREGULARITY OF THE Kα DOUBLETS IN THE ELEMENTS OF LOWER ATOMIC NUMBERS

By D. M. Bose

Abstract

In this paper attention is drawn to the recent measurements of the separation $\Delta\lambda$ of the Kα doublets of the lighter elements from Al(13) to Ge(32) by Siegbahn and Ray and by Bäcklin. From these measurements it appears that the experimentally determined values of $\Delta\nu/R(Z-3.5)^4$ deviate systematically from those calculated according to the relativity formula of Sommerfeld. This deviation is especially large in the case of the Fe group of elements. In order to account for this deviation it is supposed that the experimentally determined $\Delta\nu/R=\Delta\nu_{rel}/R+\Delta\nu_{mag}/R$. The first term on the right hand side is due to the relativity change in the mass of the radiating electron in the two orbits which produce the relativity doublet, and which can be calculated according to Sommerfeld's formula. The second term is due to the difference in the magnetic energy of the excited atom corresponding to the two different k_2 values of the radiating electron. To calculate this term use has been made of the model which was proposed by Landé to explain the relativity doublet on a magnetic basis. According to the calculations it is shown that $\Delta\nu_{mag}/R(Z-3.5)^3=\alpha^2/14$ or $3\alpha^2/32$ according to the interpretation which is given to k_2. The first formula is obtained if k_2 determines the inclination of the orbit of the radiating electron, while the second formula is obtained if k_2 determines the shape of the electron orbit. The mean of the experimentally calculated values agrees better with the second formula.

The peculiar behavior of the $K\alpha$ doublets belonging to the first transition group of elements is accounted for on the assumption that the inner magnetic fields in the atoms of these elements are large and therefore produce greater magnetic separation. It is further shown that the hypothesis, that the M_{33} sub-level is formed first in this group of elements, and then the M_{32} sub-level, which was introduced in a previous paper to explain the paramagnetic moments of these elements, receive further support from the above mentioned data.

RECENTLY the separation $\Delta\lambda$ of the Kα doublets of the lighter elements has been the object of accurate measurements by Siegbahn and Ray,[1] and by Bäcklin.[2] In Table 1, column 2, the values of $\Delta\lambda$ for the Kα doublets of the elements Al(13) to K (18) have been taken from Bäcklin and of the elements Ca(20) to Ge(32) from Siegbahn and Ray. With these values of $\Delta\lambda$ I have calculated in column 4 the values of $\Delta\nu/R(Z-3.5)^4$ for these elements and plotted them in curve II of Fig. 1. In curve I have been plotted the values of the same quantity as calculated according to Sommerfeld's relativity formula

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[1] Siegbahn and Ray, Ark. f. Mat. Asts. O. Fys. **18,** 1 (1924).

[2] Bäcklin, Zeits. f. Physik **33,** 547 (1925).

$$\frac{\Delta\nu}{R(Z-3.5)^6}=\frac{\alpha^2}{2^4}\left[1+\frac{5}{2}(Z-3.5)^2+\cdot\cdot\cdot\right]$$

It will be seen that the difference between these two sets of values of $\Delta\nu/R(Z-3.5)^4$ for different values of Z decreases continuously with increasing Z, with a sudden rise and subsequent fall as we pass along the transition groups of elements. It is the purpose of the present paper to offer an explanation of this deviation of the experimentally determined values of $\Delta\nu/R(Z-3.5)^4$ from those calculated according to Sommerfeld's formula. The explanation is based on the assumption that the difference in energy radiated by the emitting atom in the two states corresponding to the two orbits of the radiating electron is due, not only to the relativity change of mass of the latter but also to the change in the magnetic energy of the atom in these two states.

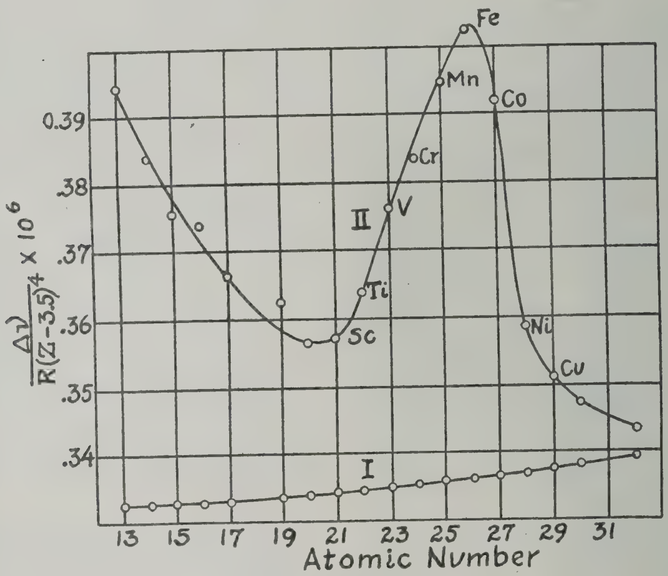

FIG. 1

We shall deal first with the continuous decrease in the value of $(\Delta\nu_{obs}-\Delta\nu_{cal})/R(Z-3.5)^4$ with increase of Z, and then we shall consider the anomalous behavior of the $K\alpha$ doublets of the elements Sc (21) to Cu (29).

I. Continuous Decrease of $(\Delta\nu_{obs}-\Delta\nu_{rel})/R(Z-3.5)^4$ with Increase of Z

The x-ray energy levels are characterized according to the notation introduced by Bohr and Coster[3] by three quantum numbers $n(k_1k_2)$, where k_1 and k_2 are the two azimuthal quantum numbers such that $k_2=k_1$ or k_1-1. The rules governing their transitions are $k_1\rightarrow k_1\pm 1$ and $k_2\rightarrow k_2\pm 1$ or k_2. In the optical spectra any one term is represented by n_{kj}, and from the rules governing the transition of k and j it can be shown that k_1 is similar to the azimuthal quantum number k and k_2 to the inner quantum number j. This similarity between x-ray and optical doublet terms has been pointed out by Landé.[4] According to the then accepted theory of the magnetic origin of optical doublets, Landé has in this paper proposed a similar explanation of these so-called relativity Kα doublets. He supposes that in an atom in which every shell has received its maximum number of electrons, the resultant moment of each is vanishingly small except in the case of the K-shell which has a resultant of one Bohr's unit of $h/2\pi$. If now from any shell containing say $2n$ electrons with the azimuthal number k one is ejected, then the remaining $2n-1$ electrons break up into a stable configuration of $2n-2$ electrons with resultant moment equal to zero, and a radiating electron with azimuthal number k . The vectorial addition of the unit moment of the atom core (K-shell) and the moment k of the radiating electron can give rise to two values of atomic moment j, viz., k and $k-1$. If we identify k_1 with k and k_2 with j we get at once an explanation of the doublet nature of the x-ray terms.

Two energy levels for which n and k_1 are the same and k_2 differs by unity from a relativity doublet. This would imply according to Landé that the atom core has two different inclinations with respect to the orbit of the radiating electron, and the term difference $\Delta\nu_{mag}$ can be calculated, according to a model proposed by Heisenberg, as follows

$$\Delta\nu_{mag}=\overline{H}o\Delta m/2\pi \qquad (1)$$

where $\overline{H}=32\pi^5m^2e^7Z^3/ch^5n^3k^2$ is the average field created by the radiating electron, and o is Larmor's precession in unit magnetic field. Δm is the change in the quantum number of the atom core, resolved parallel to the direction of $\overline{H}$.

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[3] Bohr and Coster, Zeits. f. Physik **12,** 342 (1923).

[4] Landé, Zeits. f. Physik **24,** 88 (1924).

On substituting these values in (1) we get

$$\Delta\nu_{mag}=\frac{8\pi^4me^8}{h^5c^2n^3k^2}Z^3\Delta m$$

$$=\frac{R\alpha^2}{n^3k^2}Z^3\Delta m$$

since

$$R=2\pi^2me^4/h^3 \text{ and } \alpha^2=4\pi^2e^4/h^2c^2 .$$

If we take into account the screening effect, then

$$\Delta\nu_{mag}/R(Z-3.5)^3=\alpha^2/n^3k^2 . \tag{3a}$$

We get another expression for $\Delta\nu_{mag}$ if we assume, as is necessary to explain the origin of these doublets on the relativity theory, that k_2 is the azimuthal quantum number, so that a change in k_2 represents an alteration in the shape of the orbit of the radiating electron and not in its inclination. In this case if m is the equatorial quantum number of the atom in the direction of $\overline{H}$, then the magnetic energy of the former in the field of the radiating electron is

$$\Delta E_{kin}=moL\overline{H}/2\pi$$

Keeping m constant and altering k_2, i.e. $\overline{H}$, we get

$$\Delta\nu_{mag}=\frac{\Delta E_{kin}{}^{(1)}-\Delta E_{kin}{}^{(2)}}{h}$$

$$=\frac{R\alpha^2(Z-3.5)^3m}{n^3}\left(\frac{1}{k_2'^2}-\frac{1}{k_2''^2}\right)$$

or

$$\frac{\Delta\nu_{mag}}{R(Z-3.5)^3}=\frac{\alpha^2m}{n^3}\left(\frac{1}{k_2'^2}-\frac{1}{k_2''^2}\right) . \tag{3b}$$

The corresponding expression for the relativity separation is

$$\frac{\Delta\nu_{rel}}{R(Z-3.5)^4}=\frac{\alpha_2(k_2''-k_2')}{n^3k_2'k_2''} \tag{4}$$

In the case of the Kα doublet $k_2'=1$; $k_2''=2$ while the value of k^2 in (3a) is according to Landé equal to $k^2-\frac{1}{4}=7/4$. Further in (3a) $\Delta m=1$ and in (3b) $m=1$.

Then according to (3a)

$$\Delta\nu_{mag}/R(Z-3.5)^3=\alpha^2/14 \tag{5a}$$

and according to (3b)

$$\Delta\nu_{mag}/R(Z-3.5)^3=3\alpha^2/32\ . \tag{5b}$$

From (4)

$$\Delta\nu_{rel}/R(Z-3.5)^4=\alpha^2/16\ . \tag{6}$$

The formulas (3a) and (3b) have been deduced on the assumption that the magnetic energy is due entirely to the action between the magnetic moment of the K-shell and the field due to the radiating electron. If in addition there are other shells with uncompensated magnetic moments there will then be further addition to the magnetic energy of the excited atom. This term is at present difficult to calculate.

The burden of the experimental evidence is in favor of Sommerfeld's relativity formula, and Landé himself has given up his views about the magnetic origin of the Röntgen doublets. There is no reason however to suppose that the two effects cannot exist side by side, so that the observed separation $\Delta\nu_{obs}/R$ can be represented as being given by

$$\begin{aligned}\frac{\Delta\nu_{obs}}{R}&=\frac{\Delta\nu_{rel}}{R}+\frac{\Delta\nu_{mag}}{R}\\&=(Z-3.5)^4\frac{\alpha^2}{16}\left(1+\frac{16}{14}\,\frac{1}{Z-3.5}\right)\text{ according to (5a)}\\&=(Z-3.5)^4\frac{\alpha^2}{16}\left(1+\frac{3}{2}\,\frac{1}{Z-3.5}\right)\text{ according to (5b)}\end{aligned}$$

For large values of Z, the second term on the right hand side is negligible in comparison to the first, and it is in this region that Sommerfeld's formula has been so well experimentally verified. While for small values of Z, i.e., in the region studied by Siegbahn and Ray and by Bäcklin, the second term is no longer negligible, and we have then, according to (5a),

$$\frac{\Delta\nu_{obs}-\Delta\nu_{rel}}{R(Z-3.5)^3}=\frac{\Delta\nu_{mag}}{R(Z-3.5)^3}=\frac{\alpha^2}{14}=\frac{5.31\times10^{-5}}{14}=3.8\times10^{-6}$$

and according to (5b) the same expression has the value $3\alpha^2/32$ or 4.97×10^{-6}

In Table I, I have subtracted from the observed values of $\Delta\nu/R$, the values of $\Delta\nu_{rel}/R$ calculated according to Sommerfeld's formula, and have called these differences $\Delta\nu_{mag}/R$. According to the view that is taken of the azimuthal quantum number k_2, the value of $\Delta\nu_{mag}/R(Z-3.5)^3$ ought to be either 3.8×10^{-6} or 4.97×10^{-6}.

In column VII, I have placed the calculated values of this quantity for the elements Al(13) to Ge(32). Leaving for the present the transition group of elements Sc(21) to Cu(29), we find that with the exception of the very low value for Zn(30) the other elements give values for this quantity of the expected magnitude. Omitting Zn, the mean value is found to be 4.78×10^{-6}, which is very near to the value calculated according to 5(b). This would imply that so far as the magnetic energy of the atom is concerned, the second azimuthal quantum number k_2 represents the shape of the orbit of the radiating electron, and not its inclination to the atom core.

TABLE I

Z	$\Delta\lambda$	$\Delta\nu/R$	$\dfrac{\Delta\nu}{R(Z-3.5)^4}$	$\Delta\nu/R$ (rel)	$\Delta\nu/R$ (mag)	$\dfrac{\Delta\nu_{mag}}{R(Z-3.5)^3}\times10^6$
13Al	2.44	0.03139	0.3943	0.02706	0.00433	5.05
14Si	2.58	0.04651	0.3838	0.04037	0.00614	5.32
15P	2.72	0.06570	0.3759	0.05814	0.00756	4.97
16S	2.88	0.09131	0.3742	0.08122	0.01009	5.05
17Cl	2.97	0.12150	0.3660	0.1106	0.0109	4.43
19K	3.21	0.20950	0.3631	0.1925	0.0170	4.57
20Ca	3.26	0.26440	0.3570	0.2475	0.0169	3.76
21Sc	3.37	0.33560	0.3576	0.3136	0.0220	4.11
22Ti	3.45	0.41780	0.3643	0.3920	0.0258	4.07
23V	3.60	0.52550	0.3763	0.4845	0.0410	5.54
24Cr	3.89	0.67900	0.3836	0.6064	0.0726	8.31
25Mn	4.08	0.84500	0.3949	0.7180	0.1270	12.77
26Fe	4.22	1.0250	0.4019	0.8624	0.1626	14.28
27Co	4.19	1.1920	0.3920	1.027	0.1650	12.72
28Ni	3.90	1.2920	0.3588	1.214	0.078	5.30
29Cu	3.86	1.4810	0.3514	1.430	0.051	3.08
30Zn	3.82	1.6890	0.3475	1.670	0.019	1.02
32Ge	3.91	2.2650	0.3439	2.243	0.022	5.09

II. THE ANOMALOUS BEHAVIOR OF THE Kα DOUBLETS OF THE ELEMENTS Sc(21) TO Cu(29)

The view which has been considered above receives further support when we consider the anomalous behavior of the Kα doublets of the transition group of elements which are strongly paramagnetic. According to the scheme of distribution of electrons in the different atomic sub-levels proposed by Stoner,[5] it is supposed that every such sub-level is characterized by the numbers n_{kj}, and the maximum number of electrons which can occupy any one of them is $2j$. In the first transition group of elements from Sc(21) to Cu(29), it is supposed that the two inner 3-quanta sub-levels M_{32} and M_{33} are built up with 4 and 6 electrons respectively. In a previous paper,[6] I have shown that from magnetic evidences it can be concluded that the M_{33} sub-level is first completed at Fe(26) and then the M_{32} sub-level is completed between Co(27) and Cu(29). In order to explain the experimental values of the magneton numbers of the atoms and ions of these elements, it had to be assumed that the M_{32} electrons move in a sense opposite to those of the M_{33} ones. It is at once evident that in the atoms of these elements strong inner magnetic fields exist, and in calculating the magnetic energy of the excited atom we have to take into consideration not only the energy of the atom core (i.e. of the K-shell) with respect to the magnetic field of the radiating electron, but also of the freshly formed M_{32} and M_{33} shells, and we can see why in these elements the value of $\Delta\nu_{mag}/R$ is large. In Fig. 2, I have plotted the values of $\Delta\nu_{mag}/R(Z-3.5)^3$ as a function of Z, and it will be noticed that the curve bends sharply upwards at Ca(20) and reaches its maximum at Fe(26), and then it bends downwards and reaches a minimum at Zn(30).

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[5] Stoner, Phil. Mag. **48,** 719 (1924).

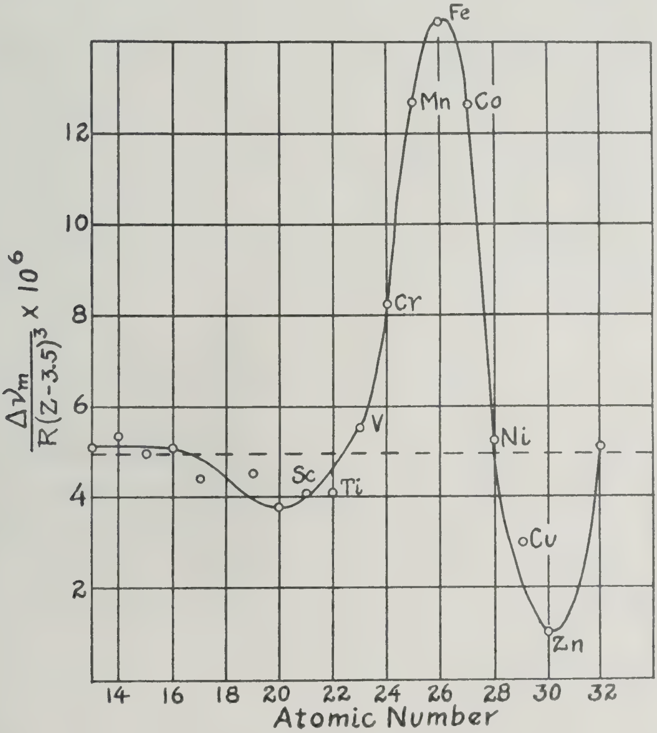

FIG. 2

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[6] Bose, Zeits. f. Physik 35, 213 (1925).

It seems as if the inner magnetic field reaches its maximum value when M_{33} sub-level is completed at Fe(26), and that this field is gradually neutralized by the one due to the motion of the electrons in the M_{32} orbits. We have thus an independent verification of the successive formation of the M_{33} and M_{32} sub-levels in these elements, a hypothesis which was assumed in a previous paper to explain certain magnetic effects.

Here an interesting question arises as to the resultant value of the magnetic moment of the six electrons in the M_{33} sub-level in the atoms of Fe(26) and the other heavier elements of this group. From spectroscopic evidences Sommerfeld and his co-workers[7] have concluded that the magneton number of Fe, Co, and Ni are 6, 6 and 5 respectively. These values do not at all agree with the values of the atomic moments found by Gerlach[7] for the elements Fe, Ni and Cu, which were found to be 0, 2 and 1 magnetons respectively. In the previous paper,[6] I have tried to calculate the magnetic moments of these elements and their ions from the following distribution of electrons.

	M_{32}	M_{33}	N_{11}
Fe:	–	6	2
Co:	1	6	2
Ni:	2	6	2
Cu:	4	6	1

The assumptions made were (i) that the magneton number is $M_{33}+N_{11}+M_{32}$, (ii) when any sub-level has received its maximum number of $2j$ electrons its resultant moment is zero. On these assumptions the atomic moments of the elements Fe, Ni and Cu come out to be 0, 2 and 1 respectively in agreement with Gerlach's results. On the other hand if we alter (ii) and suppose that the M_{33} sub-level always contributes 6 magnetons to the total moment of the atom, then for the elements Fe, Co and Ni the values of the magneton numbers come out to be 6, 5, 4 respectively which are close enough to the spectroscopically determined values of 6, 6, and 6. In the case of the $K\alpha$ doublets of these elements, we have similarly to suppose that the magnetic field produced by the motion of the electrons in the M_{33} orbits rises to its maximum value in Fe(26) and that this field is only compensated by the contrary one produced by the 4 electrons moving in the M_{32} orbits in Cu(29). Thus in general the magnetic energy of the excited atom is due to the magnetic interaction of the radiating electron with the different shells in the atom. The contributions made by each of them is at present difficult to calculate. If the rather low value of $\Delta\nu_{mag}/R(Z-3.5)^3$ for

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[7] For references see (6).

Zn(30) which was noticed previously is not due to experimental error, then it may probably be attributed to the fact that in Zn the N_{11} shell is completed.

Similar periodic variation in the sepration $\Delta\lambda$ for the Lα doublets of the elements Nb(41) to Ur(92) has been tabulated by Ray,[8] and may also be attributed to magnetic origin. The first of these periods is due to the second transition group of elements from Nb(41) to Pd(46), in which the N_{32} and N_{33} sub-levels are completed. The separations $\Delta\lambda$ for all the elements of this group are not contained in Ray's paper, and the order of accuracy in the measurement is not so great as that for the Kα doublets. The maximum separation obtained is due to the Lα doublet of Mo(42) the next being that of Ru(44). If these measurements are correct then it would indicate that the N_{32} sub-level is completed first and then the N_{33}, contrary to the order in which the M_{32} and M_{33} sub-levels are formed.

In conclusion I wish to express my thanks to Messrs. H. P. De and R. Mukherjee for helping me with the calculations contained in this paper.

University College of Science,
Department of Physics,
Calcutta, India,
December 22, 1925.

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[8] Ray, Phil. Mag. **48,** 707 (1924).

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THE K EMISSION SPECTRA FOR ELEMENTS TIN (50) TO HAFNIUM (72)

BY J. M. CORK AND B. R. STEPHENSON

ABSTRACT

Using an x-ray tube and transmission spectrograph as previously described, measurements were made of the K series emission wave-lengths of elements from Sn (50) to Hf (72), except Xe (54) and Ho (67). The β line is resolved for most of the elements into two components β' and β, having a wave-length difference of about .76 x-units. The wave-length difference between the α' and α lines varies from about 4.4 x-units for tin to 4.84 x-units for hafnium. This doublet difference when plotted with atomic number gives a curve with slight irregularities for groups of points, which may bear a relation to the method of adding additional electrons in the process of atom building.

THE K series emission wave-lengths for the elements Sn (50), Sb(51) and Te(52) have been measured by Leide.[1] For the elements Ba(56) to Nd(60) and Sa(62), Gd(64), Dy(66) and Er(68), measurements were reported by one of us.[2] In these measurements it was later found that an error existed due to an inaccuracy in the scale of the expansion micrometer gauge used to measure the distance between the slit and photographic plate in the x-ray spectrograph. When proper correction is made the previously published values are found to have a slight consistent error. More plates have, however, been taken for all these elements on the larger spectrograph used in this investigation. Liede[3] has recently published wave-length values for many of the K series lines of some additional elements.

If measurements for successive elements are to be compared, it is desirable that they be made with the same spectrograph. In the present paper the K emission spectra of all elements from Sn(50) to Hf(72) with the exception of Ho(67) and Xe(54) have been investigated.

APPARATUS

X-ray tube. The x-ray tube was similar in construction to that previously described[4], having ground joints at both anode and cathode ends. The compounds containing the elements under investigation were placed on the face of the water cooled target by first applying to the target face a thin coating of shellac and then covering it with a thin coating of the powder. The whole end of the target was then heated to expel the volatile matter. One application of material in this way was generally sufficient for the necessary exposures.

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[1] See Siegbahn, Spectroscopy of X-Rays, 1925.

[2] Cork, Phys. Rev. **25**, 197 (1925).

[3] Leide, Dissertation, Lund, (1925).

[4] Stephenson and Cork, Phys. Rev. **27**, 138 (1926).

X-ray spectrograph. The x-ray spectrograph used in this investigation has been previously described.[4] The large distance (75.593 cms) between the slit and the photographic plate resulted in a very good resolution of the K series lines, so that the β line which normally appears as a broad single line showed as a doublet. A calcite crystal was used. The grating space assumed in the computations, since the basement room in which the experimental work was performed was uniformly constant at about 22°C, was the value given by Siegbahn and Compton at 22°C, 3.02916A. No correction is made for the refraction of x-rays by the crystal material.

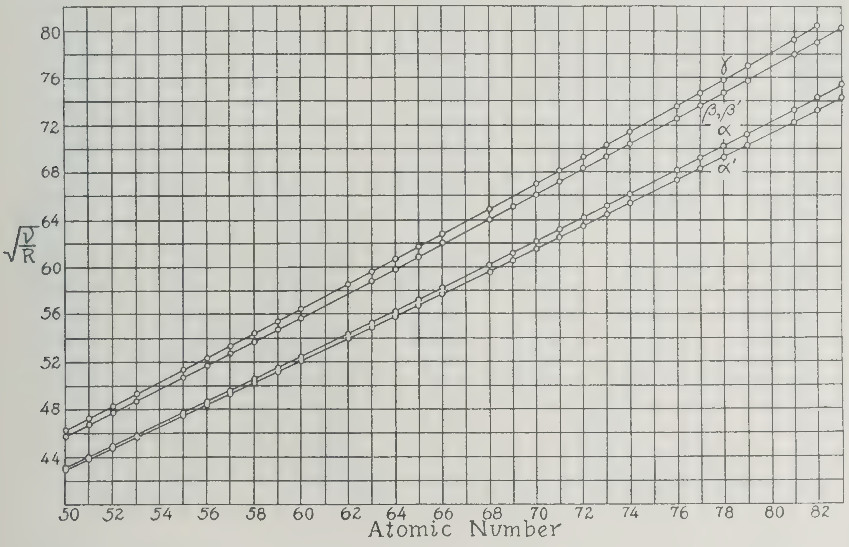

Fig. 1. Values of $\sqrt{\nu/R}$ for K series lines plotted against atomic number.

Results

Table I presents a complete summary of the data obtained. Along with the wave-length values are given the frequency numbers ν/R and the square root of ν/R where ν is the reciprocal of the wave-length in cms and R is the Rydberg number 109,737. Fig. 1 shows the square root of ν/R plotted with atomic number. In Table II are recorded values for the two components of the β line (β' and β) for all of the elements except the first three. Most of the rare earth compounds used were not chemically pure but contained neighboring elements as impurities so that overlapping spectra were obtained. In only one case, however, did lines occur so close together as to make the measurement of one of

TABLE IA

Summary of data for K series emission lines, $K\alpha$ and $K\alpha'$

		α'			α	
Element	λ	ν/R	$\sqrt{\nu/R}$	λ	ν/R	$\sqrt{\nu/R}$
50Sn	494.06	1844.4	42.947	489.66	1861.1	41.139
51Sb	474.00	1922.5	43.846	469.54	1940.8	44.054
52Te	455.04	2002.6	44.746	450.51	2022.8	44.975
53I	436.94	2085.5	45.668	432.43	2107.3	45.905
55Cs	403.98	2255.7	47.485	399.48	2281.1	47.761
56Ba	388.91	2343.1	48.404	384.31	2371.1	48.692
57La	374.60	2432.6	49.321	369.96	2463.1	49.630
58Ce	360.97	2524.5	50.242	356.37	2557.1	50.567
59Pr	348.05	2618.2	51.169	343.40	2653.6	51.513
60Nd	335.96	2712.4	52.081	331.31	2750.5	52.445
62Sa	313.20	2909.5	53.940	308.54	2953.4	54.346
63Eu	302.69	3010.5	54.868	297.99	3058.1	55.300
64Gd	292.41	3116.4	55.825	287.73	3166.9	56.275
65Tb	282.94	3220.7	56.751	278.19	3275.7	57.234
66Dy	273.64	3330.1	57.707	268.87	3389.2	58.217
68Er	256.72	3549.6	59.578	251.99	3616.2	60.135
69Tm	248.61	3665.4	60.543	243.87	3736.7	61.129
70Yb	240.99	3781.3	61.493	236.22	3857.7	62.111
71Lu	233.58	3901.3	62.461	228.82	3982.4	63.107
72Hf	226.53	4022.7	63.424	221.73	4109.8	64.108

TABLE IB

Summary of data for K series emission lines, $K\beta$, β', and $K\gamma$

		β', β (ave)			γ	
Element	λ	ν/R	$\sqrt{\nu/R}$	λ	ν/R	$\sqrt{\nu/R}$
50Sn	434.68	2096.4	45.786	425.13	2143.5	46.298
51Sb	416.42	2188.4	46.780	407.20	2237.9	47.306
52Te	399.29	2282.2	47.772	390.49	2333.6	48.308
53I	383.54	2376.0	48.745	374.61	2432.5	49.320
55Cs	353.99	2574.2	50.737	345.16	2640.5	51.386
56Ba	340.56	2675.8	51.726	332.22	2742.9	52.370
57La	327.68	2781.0	52.735	319.66	2850.7	53.392
58Ce	315.37	2889.5	53.756	307.70	2961.5	54.419
59Pr	304.00	2997.6	54.751	296.25	3076.0	55.462
60Nd	293.13	3108.7	55.756	285.73	3189.3	56.474
62Sa	272.88	3339.5	57.788	265.75	3427.5	58.545
63Eu	263.47	3458.8	58.811	256.45	3553.4	59.611
64Gd	254.33	3581.0	59.859	247.62	3680.1	60.664
65Tb	245.90	3705.8	60.875	239.12	3810.9	61.733
66Dy	237.49	3837.1	61.945	231.28	3940.1	62.770
68Er	222.58	4094.2	63.986	216.71	4205.1	64.847
69Tm	215.23	4234.0	65.069			
70Yb	208.75	4365.4	66.071	203.22	4484.1	66.963
71Lu	202.12	4508.7	67.146	196.49	4637.7	68.100
72Hf	195.49	4661.4	68.275	190.42	4785.5	69.178

them impossible. The γ line for Tm(69) was overlapped by the β line for Yb(70) which was found as an impurity in many of the compounds.

TABLE II

Values for K series β' and β lines.

Element	β'			β		
	λ	ν/R	$\sqrt{\nu/R}$	λ	ν/R	$\sqrt{\nu/R}$
53I	383.92	2373.6	48.720	383.15	2378.4	48.769
55Cs	354.36	2571.5	50.710	353.62	2576.9	50.763
56Ba	340.89	2673.2	51.700	340.22	2678.5	51.752
57La	328.09	2777.4	52.701	327.26	2784.5	52.769
58Ce	315.72	2886.2	53.725	315.01	2892.8	53.787
59Pr	304.39	2993.7	54.715	303.60	3001.5	54.786
60Nd	293.51	3104.7	55.720	292.75	3112.7	55.791
62Sa	273.25	3334.9	57.749	272.50	3344.1	57.828
63Eu	263.86	3453.6	58.767	263.07	3463.9	58.855
64Gd	254.71	3577.7	59.814	253.94	3584.4	59.904
65Tb	246.29	3699.9	60.827	245.51	3711.7	60.924
66Dy	237.87	3830.9	61.895	237.10	3843.3	61.995
68Er	223.00	4086.4	63.925	222.15	4102.0	64.047
69Tm	215.58	4227.0	65.015	214.87	4241.0	65.123
70Yb	209.16	4356.8	66.006	208.34	4373.9	66.136
71Lu	202.52	4499.6	67.079	201.71	4517.7	67.214
72Hf	195.83	4653.3	68.216	195.15	4669.5	68.334

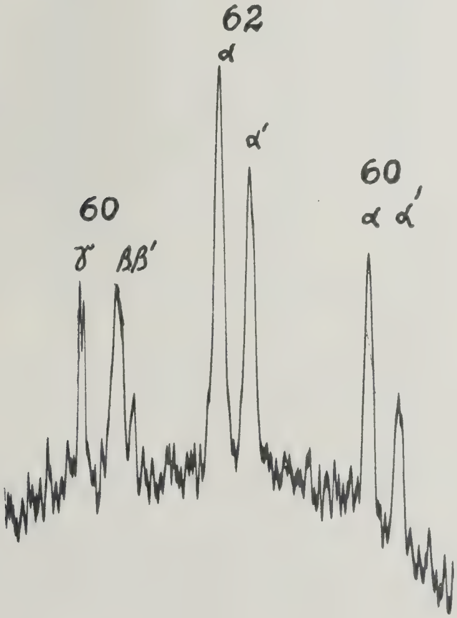

Fig. 2. Micro-photogram of K series lines of Sa(62) and Nd(60).

Fig. 2 shows a typical micro-photogram of a portion of one of the plates, which shows the presence of the elements Sa(62) and Nd(60).

Although the curve of the micro-photogram gives some notion of the relative intensity of the lines, it cannot be taken as an absolute measure because several factors, such as inequality in exposure for the different wave-lengths, non-linear density-exposure relation for the photographic film, etc., render the ordinates inaccurate as measures of intensity.

The lines were photographed on each side of the zero position and the distance between the same spectral line on opposite sides was measured. In this spectrograph a distance between lines of 10 cms corresponded to a wave-length of about 400 x-units. The α and α' lines were very sharp and well defined and their distance apart readily measurable to .01 mm involving a probable error of ±.04 x-units. While the β line is normally very broad the components when resolved are more clearly defined. The γ line is somewhat diffuse and rather weak in intensity unless the α lines are over exposed, hence the error for the β and γ lines may be considerably greater than for the α lines.

Table III

Some wave-length differences between K series lines.

Element	$\lambda_{\alpha'}-\lambda_\alpha$	$\lambda_\beta-\lambda_\gamma$	$\lambda_{\beta'}-\lambda_\beta$
50Sn	4.40	9.55	——
51Sb	4.46	9.22	——
52Te	4.53	8.80	——
53I	4.51	8.93	0.77
55Cs	4.50	8.83	0.74
56Ba	4.60	8.34	0.67
57La	4.64	8.02	0.83
58Ce	4.60	7.67	0.71
59Pr	4.65	7.75	0.79
60Nd	4.65	7.40	0.75
62Sa	4.64	7.13	0.75
63Eu	4.70	7.02	0.79
64Gd	4.68	6.71	0.77
65Tb	4.75	6.78	0.78
66Dy	4.77	6.21	0.77
68Er	4.73	5.87	0.85
69Tm	4.74	——	0.71
70Yb	4.77	5.53	0.82
71Lu	4.76	5.63	0.81
72Hf	4.80	5.07	0.68
73Ta	4.85	5.39	——
74W	4.83	5.24	——
76Os	4.86	4.86	——
77Ir	4.85	4.74	——
78Pt	4.81	4.83	——
79Au	4.87	4.76	——
81Tl	4.86	4.72	——
82Pb	4.88	4.81	——
83Bi	4.84	——	——

Column 3 of Table III shows the results obtained by subtracting the wave-length of the α line from that of the α' line for each of the elements. This wave-length difference is associated with the energy difference between the L_2 and L_3 electron levels. The same results are shown graphically in Fig. 3. It may be observed that there is in general an increase in $\Delta\lambda$ with atomic number from about 4.40 x-units for tin to 4.80 for hafnium. In the region of the rare earth elements, however, certain groups of points seem to show a systematic deviation from a smooth curve by amounts slightly greater than the probable experimental error. These changes in slope may have significance in the way electrons are added in the process of atom building. An increase in slope might be interpreted as an indication that the electron is added in such a way that its screening effect is greater by an unusual amount upon the L_3 level than upon the L_2 level. This might be the case if the electron is added in the very eccentric orbits such as the 4_1, 5_1, 6_1, or perhaps 4_2, 5_2, 6_2 levels since in these the electron penetrates close to the nucleus during a portion of its path. Thus an upward slope might be expected for the elements 55 and 56 since for these elements the last electrons are added in a 6_1 orbit. However, for 57 et seq. it is presumed electrons are added in such a way as to fill up the vacancies in the four quantum or five quantum orbits. According to the plan of Stoner these unfilled orbits are not the most eccentric while in the Bohr and Coster arrangement two electrons must be added to each of the eccentric 4_1, 4_2, 5_1, and 5_2 orbits. Too much confidence must not be placed herein because the deviations are of the

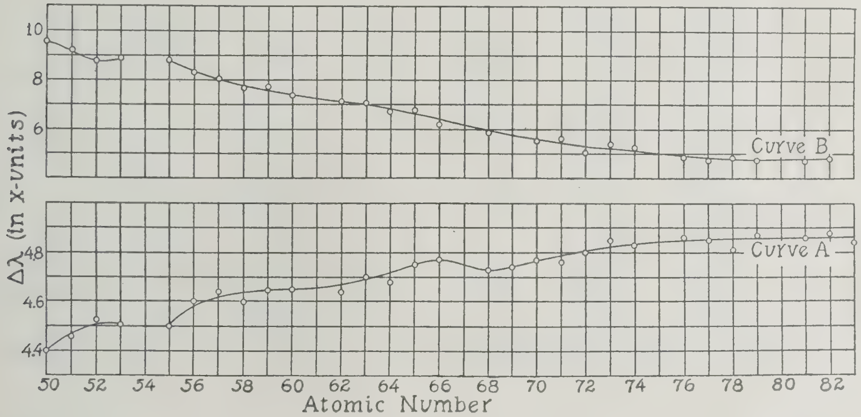

Fig. 3. Wave-length differences, $(\alpha'-\alpha)$ and $(\beta-\gamma)$ plotted against atomic number.

same order of magnitude as the experimental error. Siegbahn and Ray[5] have observed the variation in this doublet difference for lighter elements showing very noticeable irregularities. In the region of the alkali metals K and Ca the curve had a negative rather than positive slope while for Rb and Sr the slope was positive. The L $\alpha\alpha'$ doublet has also been investigated by Ray[6] for the elements mentioned in this paper and periodic deviations from a smooth curve observed.

TABLE IV

Element	λ_γ	λ_{Kabs}*	$\lambda_\gamma - \lambda_{Kabs}$*	$\Delta\nu/R$ $(L_\beta - L_\alpha')$	$\Delta\nu/R$ $(K_\alpha - K_\alpha')$
50Sn	425.13	423.94	1.19	16.72	16.7
51Sb	407.20	406.09	1.11	18.30	18.3
52Te	390.49	389.26	1.23	20.00	20.2
53I	374.61	373.44	1.17	21.70	21.8
55Cs	345.16	344.07	1.09	25.59	25.4
56Ba	332.22	330.70	1.52	27.74	28.0
57La	319.66	318.14	1.52	30.01	30.5
58Ce	307.70	306.26	1.44	32.05	32.6
59Pr	296.25	295.1	1.15	35.02	35.4
60Nd	285.73	284.58	1.15	37.86	38.1
62Sa	265.75	264.4	1.3	43.95	43.9
63Eu	256.45	254.8	1.6	47.17	47.6
64Gd	247.62	246.2	1.4	50.64	50.5
65Tb	239.12	237.6	1.5	54.36	55.0
66Dy	231.28	230.1	1.2	58.24	59.1
68Er	216.71			66.81	66.6
69Tm				71.27	71.3
70Yb	203.22	201.6	1.6	76.08	76.4
71Lu	196.49	195.1	1.4	81.11	81.1
72Hf	190.42			86.76	87.1

* Siegbahn, English Edition, 1925.

Column 4 of Table III shows in a similar way the result obtained by forming the wave-length difference between the average β and γ lines for each element. This wave-length difference decreases in general with atomic number from 9.55 x-units for tin to 5.07 for hafnium. These results are also shown graphically in Fig. 3, curve *B*. This wave-length difference is associated with the energy difference between the $M_{2,3}$ and $N_{2,3}$ orbits. It may be observed that here also certain groups of points deviate somewhat from a smooth curve. This is observable particularly well in the region of elements 53 to 57.

Column 5 of Table III shows the wave-length differences for the β' and β lines. This wave-length difference is apparently constant, except for experimental error, and has an average value of .76 x-units.

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[5] Siegbahn and Ray, Arkiv. för Matematik, Astronomie och Fysik, **18**, 19; also Siegbahn, Spectroscopy of X-Rays, 1925.

[6] Ray, Phil. Mag. **48**, 707 (1924).

Table IV, column 5, shows a summary of the wave-length difference between the γ line and the K absorption edge for each element. The square root of the frequency difference between the K absorption edge and the γ line should, when plotted with atomic number, give a line of positive slope with abrupt changes in slope in the region of the rare earth elements as predicted by Bohr and Coster. As these absorption measurements have been made by different observers and some are undoubtedly in error this curve is not presented. In columns 6 and 7 the frequency difference for the Kα doublet is compared with that for the Lβ and Lα' lines. The agreement is in most cases fairly close.

UNIVERSITY OF MICHIGAN,
December 5, 1925.*

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* Received February 18, 1926.—Ed.

THE L ABSORPTION LIMITS OF TUNGSTEN: PHOTOMETRIC MEASUREMENTS

By C. B. Crofutt

Abstract

In a previous paper both the absorption and emission spectra of tungsten were photographed simultaneously on the same plate. It has since seemed advisable to make a photometric analysis of the original plates showing the L absorption bands. The results give for L_1, 1.2117A, and for L_2, 1.0708A, as compared with the former eye measurements of 1.2122A and 1.0716A, though the last are regarded by the author as more reliable. The mean variation in the measurements is less than .0002A. L_1 is clearly between β_5 and β_{10} and L_2 between γ_6 and γ_2, indeed between γ_6 and a new line, 1.0699A.

IN A previous work[1] both the absorption and emission spectra of tungsten were photographed simultaneously on the same plate. Because accuracy in the measurement of the absorption limits is important, it seemed advisable to measure them on the original plates by means of photometric curves.

The photomicrograph[2] used was built and used at the University of Iowa. A complete description will be published later. Briefly it consists of a suitable lens system whereby a narrow beam of light (from .06 mm. to .12 mm) can be passed through the photographic plate and allowed to fall upon one junction of a thermocouple connected to a sensitive galvanometer, the deflection of which is a measure of the transparency of the plate.

It soon developed that, while the plates appeared very good to the eye and under low magnification, they were not of sufficient quality to give photometric curves in which the order of magnitude of the irregularities was less than the variations to be measured. These local irregularities were not entirely due to the individual grains of silver in the emulsion but to a great extent to the lack of uniformity of the emulsion. There were spots on the plate of the order of magnitude of a square millimeter which would differ in density from a neighboring one by fifty percent. Unfortunately the thermocouple junction had a length of sensitive spot of the order of only a millimeter.

Because of the irregularities in a plate, a single photometric curve could not be used to locate the absorption bands with certainty. This made necessary several curves over the same region with the setting displaced parallel to the spectrum lines. These curves were then averaged graphically. The resulting curves, called average curves, are the ones shown. No curve here presented and showing an absorption band is the average of less than two.

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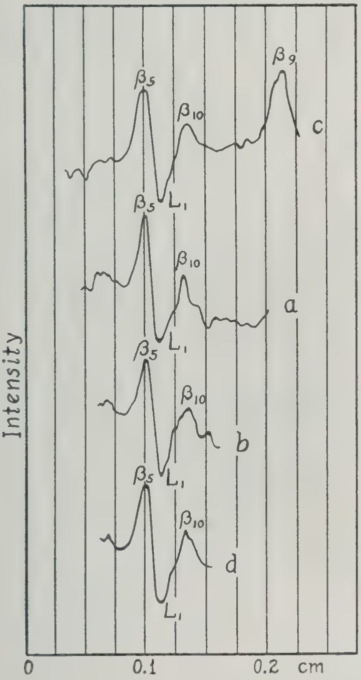
[1] C. B. Crofutt, Phys. Rev. **24**, 9 (1924).

[2] The microphotometer is a modification of that described by Harrison, J.O.S.A. & R.S.I., **10**, 157 (1925). In this article are references to the literature.

The results are shown in Figs. 1, 2 and 3. Fig. 1 shows the region in the neighborhood of the L_1 absorption band. Curves *a*, *b* and *c* are the average of two or three parallel curves obtained from three separate exposures. Curve *d* is the average of the three curves *a*, *b* and *c*.



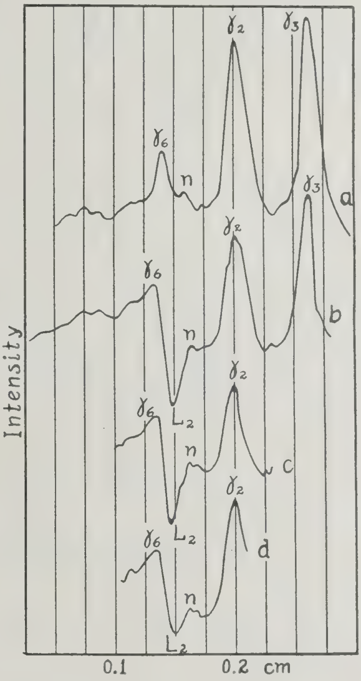


Fig. 1. Average photometer curves showing L_1 absorption.
Fig. 2. Average photometer curves: (a) emission, (b), (c), (d) emission and L_2 absorption.

Fig. 2 shows the region in the neighborhood of the L_2 absorption band. Curve *a* shows the emission spectrum without the absorption band. It will be seen that the line marked *n* is one of the new lines reported in the previous paper. Curves *b* and *c* were taken under identical conditions except that the widths of the beams of light passing through the plate were 0.1 mm and .06 mm, respectively. Curve *d* is the average of four curves taken from two plates.

Fig. 3, the average of three parallel curves, shows the region in the neighborhood of the L_3 absorption band. It is the least satisfactory of the three.

All curves in Figs. 1 and 2 have been translated so that corresponding points on the curves have the same abscissas. The peaks of β_5 and γ_2 have been taken as corresponding points for this purpose.

It is seen that the absorption L_1 falls between the emission lines β_5 and β_{10} and that L_2 falls between the emission lines γ_6 and γ_2. Since the wave-lengths of β_5, β_{10}, γ_6 and γ_2 as previously reported have not been questioned, these curves show conclusively that L_1 falls between the wave-lengths 1.2133A and 1.2099A and that L_2 falls between wave-lengths 1.0723A and 1.0659A. These wave-lengths are those measured assuming the grating space of rock salt to be 2.8140A.

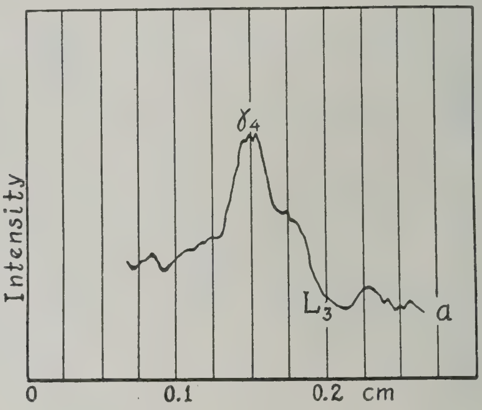


Fig. 3. Average photometer curve showing L_3 absorption.

It is noticed that all the curves show on the short wave side of the absorption limit a decrease of radiation below that of the continuous spectrum in the absence of the absorber. These are the "white lines" referred to in the literature and apparently found only with photography.

TABLE I

Interpolated values of wave-lengths of L_1 and L_2 absorption bands

	L_1	L_2			
	Fig. 1(d)	Fig. 2(b)	Fig. 2(c)	Fig. 2(d)	Ave.
Long wave-length edge:	1.2116	1.0709	1.0709	1.0708	1.0709
Peak:	1.2120	1.0708	1.0710	1.0708	1.0709
Short wave-length edge:	1.2116	1.0704	1.0707	1.0706	1.0706
Average:	1.2117				1.0708

In the judgment of the author the photometer curves do not furnish as accurate a measurement of the wave-lengths as those already published which were obtained by direct measurement of the plates, using a dividing engine and a low powered microscope. However, on account of the importance of accurate measurements it seemed advisable to determine the wave-lengths corresponding to absorptions L_1 and L_2 from the curves. This was done by interpolation, using β_5 and β_{10} as reference lines for L_1 and γ_6 and γ_2 as reference lines for L_2 with the wave-lengths of the four as given in the preceding paragraph. The measurements for these interpolations were taken from three different points on the lines and bands: the long wave-length edges, the peaks, and the short wave-length edges. The results are shown in Table I. These results are compared with previous results in Table II. It is seen that the wave-lengths obtained from the photometric measurements of the plates are somewhat shorter than the previous results.

TABLE II

Comparison of results

		L_1	L_2
Duane	:	1.2140	1.0730
Direct Measure	:	1.2122	1.0716
Photometric Meas.	:	1.2117	1.0708

In conclusion, photometric curves have been obtained showing the L_1, the L_2, and the L_3 absorptions of tungsten. The results are in agreement with the results previously reported, which are regarded by the author as the more reliable.

I wish to acknowledge indebtedness to the members of the staff of the physical laboratory at the University of Iowa and especially to Professor Stewart, for their interest in the work.

UNIVERSITY OF ARKANSAS,
January 25, 1926

MAY, 1926 PHYSICAL REVIEW VOLUME 27

NATURAL IONIZATION IN GASES

By James W. Broxon

Abstract

Measurements of the *pressure variation* of the natural ionization in air, nitrogen, oxygen and carbon dioxide contained in a steel sphere of one foot inside diameter, made by H. F. Fruth for pressures from 1 to 75 atmospheres, were repeated with slight modifications. Results obtained corresponded with those of Fruth with the following exceptions: (1) although the pressure rate of variation of the natural ionization at high pressures was very small (0.4 to 1.0 ion/cc sec. atm.) no abrupt change in the rate of variation and no true "saturation" value of the ionization were observed; (2) no "anomalous" behavior was noted in the case of commercial nitrogen. Measurements to detect the *variation with size of chamber* were carried out with spherical iron ionization chambers of 7, 9, and 12 in. respective internal diameters. The rate of production of ions per cc at high pressures did not vary unidirectionally with the size of the ionization chambers, but was least in the 9 in. sphere. To study the *effect of the lining* the experiments were repeated with oxygen in each of the spheres lined with aluminum of 1/16 in. thickness, and in the 12 in. sphere lined with copper of 1/16 in. thickness. The aluminum lining increased the ionization at low pressures, and decreased its pressure rate of variation at high pressures. The copper lining reduced the absolute value of the ionization at high pressures. The *effect of water vapor* on the natural ionization in aged, dust-free air, or upon its variation with pressure was found to be negligible. Both the absolute and the fractional *variation of the natural ionization with time* were found to depend upon the pressure, the average value of the former during a 24 hr. period being about twice and that of the latter being about 1/5 as great in oxygen at 55.4 atm. pressure as in air at atmospheric pressure. Very slight evidence of a singly periodic diurnal variation in air at atmospheric pressure was observed. Attempts to determine the *effects of slow chemical reactions* upon the natural ionization in air and oxygen at atmospheric pressure led to negative results.

Introduction

THIS paper has to do with the ionization occurring in closed vessels apart from the action of definitely recognized and localized ionizing agents, a problem first attacked from the present point of view by C. T. R. Wilson[1] and Elster and Geitel.[2] In their work on the variation of the natural ionization with pressure, it was found by Downey[3] in the case of air, and by Fruth[4] in the cases of "purified" air and oxygen, that the natural ionization in a gas in a spherical steel container increased with the pressure until pressures of about 46 and 52 atmospheres, respectively, were attained, and remained constant as the pressures were still further increased. Fruth found a similar saturation value in the case of carbon dioxide at 61 atmospheres. His results show no such saturation value in the case of nitrogen either as prepared commercially or in the laboratory. Moreover, no saturation value was observed in the case of oxygen and nitrogen which had been mixed in approximately the same ratio as they occur in air.

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[1] C. T. R. Wilson, Proc. Camb. Phil. Soc. **11,** 32 (1900); Roy. Soc. Proc. **A68, 151** (1901).

[2] H. Geitel, Phys. Zeits. **2,** 116 (1900);
J. E. Elster and H. Geitel, Phys. Zeits. **2,** 560 (1901).

[3] K. M. Downey, Phys. Rev. **20,** 186 (1922).

[4] H. F. Fruth, Phys. Rev. **22,** 109 (1923).

It was with the particular object of further investigating the occurrence of these saturation values and of discovering the reason for the "anomalous" behavior of nitrogen, that the present work was undertaken at the suggestion of Professor W. F. G. Swann.

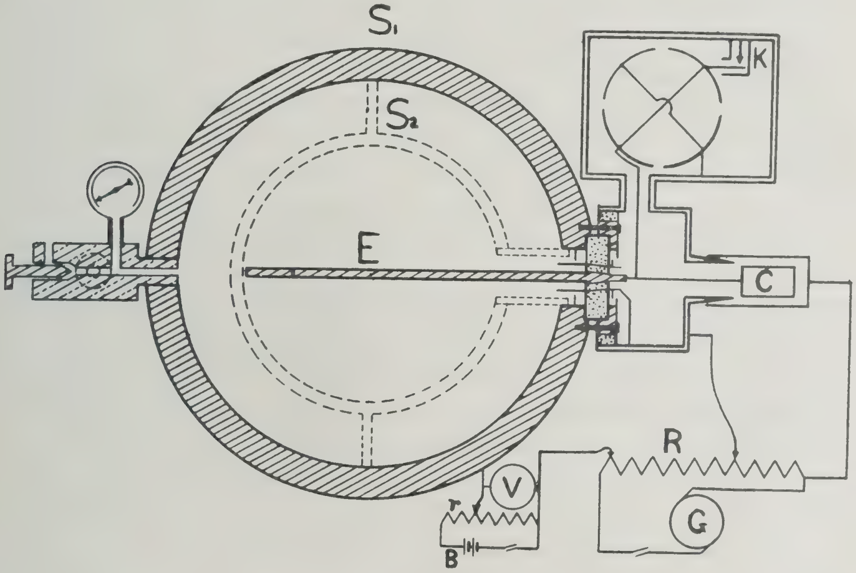

Fig. 1. Diagram of apparatus.

Apparatus and Manipulation

The ionization chamber consisted of the same iron sphere of one foot internal diameter, with walls of one inch thickness, which was used by Fruth, and the experimental arrangement corresponded closely with that described by him, certain modifications being made as shown in Fig. 1. The guard system was slightly modified, lead was substituted for the red rubber gasket, and the compensating condenser, C, was fixed. Observations and calculations were also made in essentially the same manner as in Fruth's work, all the precautions listed by him being taken in this instance.

In addition to the original sphere of 12 in. internal diameter, two iron spheres were cast, their thickness being 1/4 in. and their diameters 7 in. and 9 in., respectively. These could be inserted individually within the 12 in. sphere and held concentric with it by means of collars and a connecting pipe, as shown by the dotted S_2 in Fig. 1, E being made correspondingly shorter. As in the case of S_1, these spheres were actually cast as hemispheres and bolted together, but no attempt was made to make the inner spheres gas-tight, the pressure inside them being everywhere the same as that inside S_1.

In the present case, electrometer fibers from 2 to 5 times as sensitive as those used by Fruth were employed; three individual sets of readings were taken in practically every instance at each pressure; and the gases were passed first through the drying tube and then through the dust remover. The calibration constant, K, for a given arrangement of the ionization chamber, was usually considered at all pressures[5] to have the same value as at atmospheric pressure. In the case of carbon dioxide, however, a considerable variation was observed, and K was determined at each pressure. Saturation currents were assured by using ionization chamber potentials such that an increase of less than 0.3 percent in the currents resulted when the potentials were doubled.

No elaborate system of shielding was adopted. The thick walls of the ionization chambers themselves provided a certain amount of shielding from external radiations. In one instance, with the 9 in. sphere in position and filled with oxygen at a pressure of 200 lbs. per sq. in., measurements of the natural ionization were made before and after the placing of boxes of lead storage battery plates in the vicinity of the ionization chamber. These plates provided roughly a 6 in. lead wall subtending a solid angle of approximately $4\pi/3$ at the center of the chamber. With due consideration for its variation with time, the natural ionization could not be considered to have been decreased by more than $3\frac{1}{2}$ percent by the lead shield. An actual decrease, however, appears to have occurred.

The hydrogen and hydrogen sulphide used were formed in Kipp generators by the action of hydrochloric acid upon zinc and upon ferrous sulphide, respectively. The other gases used were purchased from commercial producing companies, with the exception of air which was compressed in the laboratory.

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[5] It should be noted at this point that throughout this paper all pressures referred to in terms of lbs per sq. in. are pressures *in excess* of atmospheric pressure.

RESULTS AND DISCUSSION

Pressure Variation. In order to determine the variation with pressure of the natural ionization in certain gases, the natural ionization occurring in air, oxygen, nitrogen and carbon dioxide was measured with the 12 in. sphere as ionization chamber, at various pressure intervals between atmospheric pressure and pressures in the neighborhood of 1000 lbs. per sq. in. The results are shown in Figs. 2, 3 and 5.

In view of the announced purpose of this research, perhaps the most noticeable feature of the results obtained is the fact that in no instance was a true saturation value observed. According to Fruth's[4] results a saturation value of the ionization should have been obtained at 53 atmospheres or about 779 lbs. per sq. in., in the cases of oxygen and of air contained in the 12 in. sphere. However, although the above pressure was exceeded by from 13.6 to 22.5 atmospheres with both oxygen and air in all the cases in which the pressure variation with these two gases was investigated, the curves in no instance became horizontal nor was there evidence of a sharp break at any point. On the other hand, all the curves obtained are smooth and are everywhere concave downward, i.e., toward the pressure-axis. It is seen, therefore, that with both air and oxygen the slopes of the P-n curves decreased gradually with pressure, so that the curves may be considered to be approaching saturation values. However, the pressure rates of change of slope at the highest pressures are very small and it is only possible to conjecture as to whether the curves would finally reach saturation values, whether their slopes would continually decrease without vanishing, or whether the curves would become straight lines with constant small slopes. The gradual decrease in the curvature of these curves together with the form of the curves for nitrogen and carbon dioxide, tend rather to persuade one toward the latter view. The pressure curves obtained with nitrogen and carbon dioxide are practically straight lines at pressures above 800 and 500 lbs. per sq. in., respectively.

In their most important aspects, the results described in this paper agree with those of Downey and Fruth. In each case investigated, with whatever gas, size of ionization chamber or nature of lining, at the highest pressures obtained the rate of increase in the natural ionization with pressure was very small, being in no case greater than one ion (of one sign) per cc per sec. per atm. The values given in Table I for the least slopes agree very well with the values of Δq given in Table II of Dr. Downey's 1922 paper for the CD portion of her curves, as well as with the final slopes of Fruth's curves apart from the horizontal portions of his curves for air and oxygen. As nearly as can be determined, if we neglect these portions of Fruth's curves, we have as the ratios of the final slopes of his curves to the final slopes of the curves in this paper for the same gases in the unlined 12 in. sphere: 1.67 for air; 1.37 for oxygen; 1.52 for nitrogen; 1.67 for carbon dioxide. If his "saturation" values be neglected, then, it would appear that the final slopes of his curves are from 1 1/3 to 1 2/3 times as large as those of curves obtained similarly in this investigation. In other words, there is very close agreement.

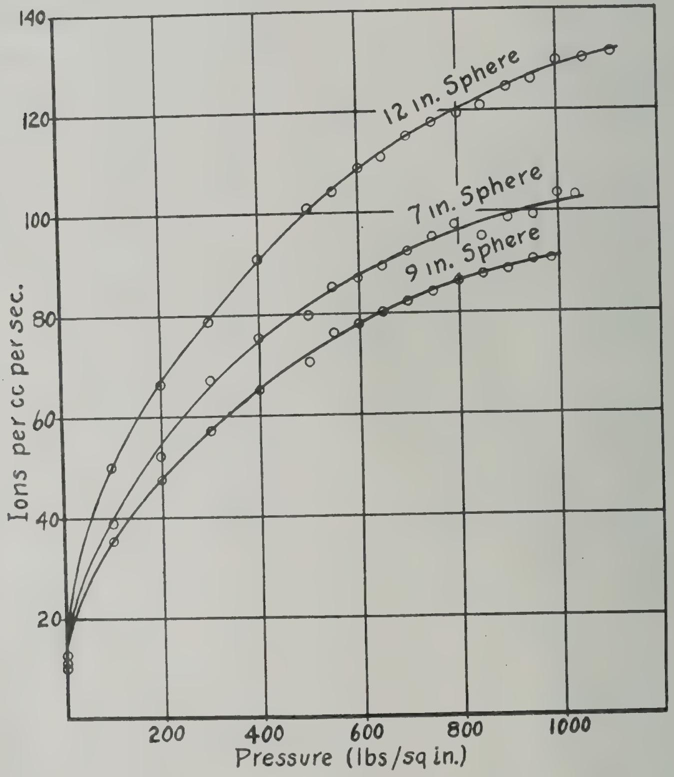

FIG. 2. Variation with pressure of the natural ionization in air.

It may be noted that some of the curves obtained by the writer are of the same general type as obtained by Wilson[6] for pressures up to 40 atmospheres. Evidence recently provided by Millikan[7] for the existence of a very penetrating cosmic radiation points toward the probability that ionization due to this source at sea level should be very small, and of about the order herein obtained per atmosphere increase of pressure at the highest pressures. Swann[8] has drawn attention to the smallness of the effect to be expected from this source.

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[6] W. Wilson, Phil. Mag. **17,** 216 (1909).

[7] R. A. Millikan, Science **62,** 445 (1925); Nature **116,** 823 (1925); Proc. Nat. Acad. Sci. **12,** 48 (1926) especially p. 51.

VARIATION WITH SIZE OF IONIZATION CHAMBER

The magnitude of the natural ionization occurring in a gas at high pressures and also its rate of variation with pressure, were found to depend upon the size of the ionization chamber. This dependence is readily seen upon inspection of Figs. 2, 3 and 4. One outstanding fact which was not expected is that at the higher pressures the curves for the 7 in. sphere lie between those for the 12 in. and 9 in. spheres. Thus the ionization (ions/cc sec.) must pass through a minimum as the size of the chamber is varied. This peculiarity exists at all pressures above 1 atm. excepting in the case of oxygen in the unlined spheres, in which

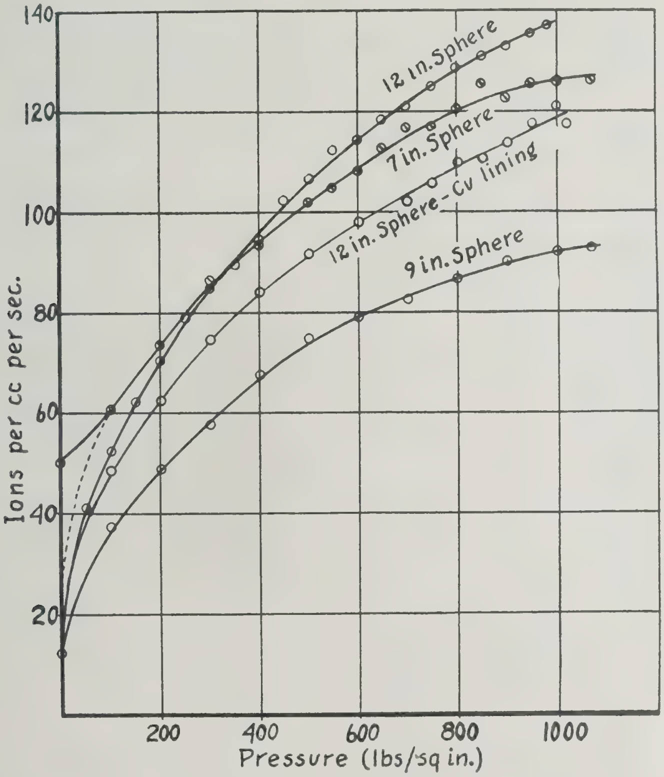

FIG. 3. Variation with pressure of the natural ionization in oxygen.

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[8] W. F. G. Swann, Nat. Res. Coun. Bull. 17, 3, 65 (1922).

case the curve for the 7 in. sphere crosses that for the 12 in. sphere and the former has an abnormally high value at atmospheric pressure. If the ionization were chiefly due to soft radiations from the walls of the ionization chamber and if the magnitude of these radiations could be considered to be proportional to the area as long as the walls were made of the same material, then an increase in the number of ions per cc per sec. should be expected to accompany a decrease in the volume with its accompanying increase in the ratio of area to volume. A theoretical discussion of these matters will appear in a subsequent publication.

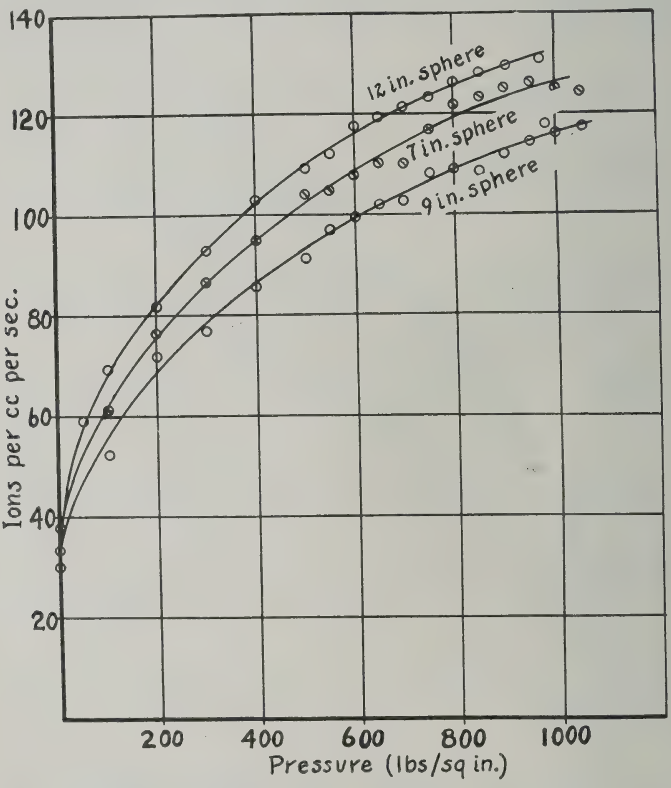

FIG. 4. Variation with pressure of the natural ionization in oxygen. Spheres lined with aluminum.

At atmospheric pressure, the rate of production of ions per cc in the 12 in. sphere was in each case slightly less than the corresponding ionization in the smaller spheres. However, without more extended series of readings with the various spheres at atmospheric pressure, this observation should not be considered to be well established.

One interesting observation is (see Table I) that the smallest slope or the least change in the number of ions per cc per sec. per atmosphere increase of pressure, apparently decreased slightly with the size of the spherical ionization chamber. The smallest value observed was about 0.18 ion/cc sec. atm. in oxygen contained in the 7 in. sphere at a pressure of 1070 lbs. per sq. in.

DEPENDENCE UPON KIND OF GAS

As has been mentioned previously, the curvature in the nitrogen and carbon dioxide curves appears to be quite definitely zero over considerable distances at their high-pressure ends. Although all the values at atmospheric pressure were of about the same magnitude, the values of the ionization in nitrogen and carbon dioxide at the higher pressures were considerably greater than the values at corresponding pressures in the other gases in the same 12 in. sphere.

It is seen upon reference to Table I that the least slopes of the oxygen and air curves are of about the same magnitude, whereas those for nitrogen and carbon dioxide are considerably greater and about equal. In fact, upon superposition of the nitrogen and carbon dioxide curves (Fig. 5), it is seen that they nearly coincide throughout, the latter being a little more concave at the lower pressures, while in the former the concavity is smaller but more persistent.

TABLE I

Least slopes of pressure-ionization curves.

Gas	Ionization Chamber	Lining	Least slope $\left(\frac{\text{ions}}{\text{cc sec. atm.}}\right)$
Air	12-in.	None	0.40
Air	9-in.	None	0.32
Air	7-in.	None	0.26
O_2	12-in.	None	0.65
O_2	9-in.	None	0.24
O_2	7-in.	None	0.18
O_2	12-in.	Al	0.50
O_2	9-in.	Al	0.41
O_2	7-in.	Al	0.40
O_2	12-in.	Cu	0.65
N_2	12-in.	None	0.97
CO_2	12-in.	None	1.00
Air + H_2O Vapor	12-in.	None	0.90

The curve for moist air shown in Fig. 5 was obtained by pouring 20 cc of distilled water into the 12 in. sphere, unlined, after which aged, dry, dust-free air was admitted to a pressure of 750 lbs per sq. in. Examination of the curve shows that there was no particular difference (so far as observations extended) between the ionization occurring in this case and that in dry air in the same chamber. Values at the higher pressures were slightly smaller in the former case than in the latter, but the divergence between the two curves is small and gradual. The final least slope of the air—water vapor curve is practically the same as that of the dry air curve at the same pressure. Therefore, water vapor evidently produces no decided effect upon the natural ionization in aged, dust-free air. It might, however, produce a considerable effect in the presence of dust particles.

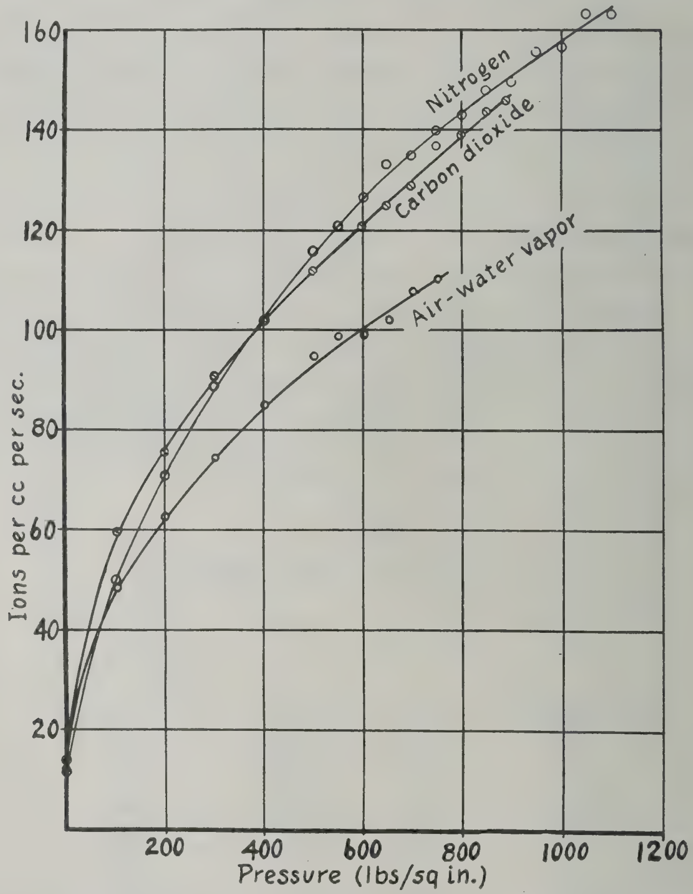

FIG. 5. Variation with pressure of the natural ionization in N_2, CO_2 and air saturated with water vapor.

Since no outstanding differences other than those mentioned above were found to exist among the values of the natural ionization or the P-n curves obtained for the various gases investigated, there evidently exists no special "anomalous" effect for nitrogen so far as this investigation is concerned. There remain, however, the larger slopes for nitrogen and carbon dioxide.

EFFECT OF LINING

The effects of the metals constituting the ionization chambers, upon the natural ionization in gases, particularly air, were early investigated by several experimenters,[9] especially by Campbell and McLennan. These investigations, however, were ordinarily carried out at atmospheric pressure. Evidence has been provided to show that the natural ionization does depend upon the material constituting the vessel, and also upon the particular sample of the material.

In Figs. 3 and 4 are the three P-n curves which were secured with oxygen in ionization chambers of practically the same size (12 in. diameter) but with different metals constituting their inner surfaces. It is seen that the two curves for the respective cases in which the iron sphere was unlined and in which it was lined with copper, start at practically the same point and have practically the same initial and the same final slope. The early intermediate curvature is rather greater in the case of the copper lined sphere, however, resulting in considerably lower values for the ionization at high pressures in this case.

With the chamber lined with aluminum, the value of the ionization at atmospheric pressure was much larger than in the other two cases. This particularly high value of the ionization at atmospheric pressure appears to have been characteristic of the aluminum lining inasmuch as it was observed with each of the three spheres (see Fig. 4). The curvature of the curve for aluminum, however, corresponds very closely with that of the curve for the copper lining for pressures below 600 lbs. per sq. in. and is more persistent than in the latter curve at greater pressures. The result, therefore, is that the aluminum curve has a smaller final least slope than do the other two curves for oxygen in the 12 in. sphere, and the final absolute value of the ionization is larger than with the copper lining.

As is shown by Fig. 4, the curves obtained with each sphere lined with aluminum are very regular and correspond closely. It might be concluded, therefore, that the aluminum gave rise to a rather bounteous supply of comparatively easily absorbable radiation. This suggests an explanation in terms of the considerable secondary cathode radiation excited by gamma radiation in substances of light atomic weight.[10] The chief effect of the copper lining appears to have been the reduction of the absolute value of the ionization at high pressures. It should be noted that radiations from the iron which could have penetrated 1/16 in. of aluminum or copper would have affected the ionization occurring with these two linings.

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[9] A. Wood, Phil. Mag. **9,** 550 (1905);
N. R. Campbell, Phil. Mag. **11,** 206 (1906);
N. R. Campbell, Camb. Phil. Soc. Proc. **13,** 282 (1906);
J. C. McLennan, Phil. Mag. **14,** 760 (1907);
J. C. McLennan, Phys. Rev. **26,** 526 (1908).

Variation with Time

The variation with time of the natural ionization in the atmosphere is of interest in connection with problems concerned with the atmospheric potential gradient, the emanation content, the magnetic intensity, etc. Wood and Campbell,[11] McKeon,[12] Strong,[13] Wright,[14] Gockel,[15] Simpson,[16] Wulf,[17] Downey,[18] and others have investigated more or less exhaustively the variation with time of the natural ionization in air at atmospheric pressure. No general agreement appears to have resulted as to whether the diurnal variation is singly or doubly periodic or whether it exists at all.

In the present investigation of the variation at atmospheric pressure there was, as is designated by the dotted curves in Fig. 6, a decided similarity between fluctuations during the first two 24-hr. periods. The large general variations partook of a single periodicity with maxima in the early afternoon and minima in the early morning. The weather was turbulent or stormy during these periods. During the third period, when the sky was comparatively clear, the above periodicity did not appear. In view of previous work it is concluded that the present work, extending over a period of only 72 hrs., contributes very little toward the solution of the daily variation problem.

From the summary in Table II, it is seen that the average deviation from the mean at atmospheric pressure was of the order of ½ ion/cc sec., or about 5 percent of the mean, whereas the largest variations were of the order of 2 ions/cc sec., or about 20 percent of the mean. Smaller fluctuations were observed by Swann[19] in the same laboratory at about the same time.

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[10] W. H. Bragg and J. P. V. Madsen, Phil. Mag. **15,** 663 (1908).

[11] A. Wood and N. R. Campbell, Phil. Mag. **13,** 265 (1907).

[12] T. F. McKeon, Phys. Rev. **25,** 399 (1907).

[13] W. W. Strong, Phys. Zeits. **9,** 117 (1908).

[14] C. S. Wright, Phil. Mag. **17,** 295 (1909).

[15] A. Gockel, Phys. Zeits. **10,** 845 (1909).

[16] G. C. Simpson and C. S. Wright, Roy. Soc. Proc. **A85,** 175 (1911).

[17] Benndorf, Dorno, Hess, v. Schweidler, Wulf, Phys. Zeits. **14,** 1141 (1913).

[18] K. M. Downey, Phys. Rev. **16,** 420 (1920).

[19] W. F. G. Swann, Jour. Franklin Inst. Oct. (1925).

Curve I of Fig. 6 shows that with oxygen at a pressure of 800 lbs. per sq. in. there was no periodicity corresponding to that at atmospheric pressure. The magnitude of the average deviation from the mean was about twice that in air at atmospheric pressure, and the magnitude of the maximum deviation was rather more than twice the largest deviation at atmospheric pressure. The average deviation from the mean at a pressure of 800 lbs. per sq. in. was only about 1 percent and the maximum deviation about 5 percent of the mean. The larger

TABLE II

Variations over 24-hr periods of the natural ionization at constant pressure.

Press.	No. of Readings	Mean no. of ions/ cc sec.	Ave. dev. from mean	Max. dev. from mean
800 lbs./in.^{2}	67	118.82	1.163	5.62
Atmos.	71	10.58	0.600	2.23
Atmos.	66	11.21	0.695	2.02
Atmos.	72	10.71	0.427	1.24

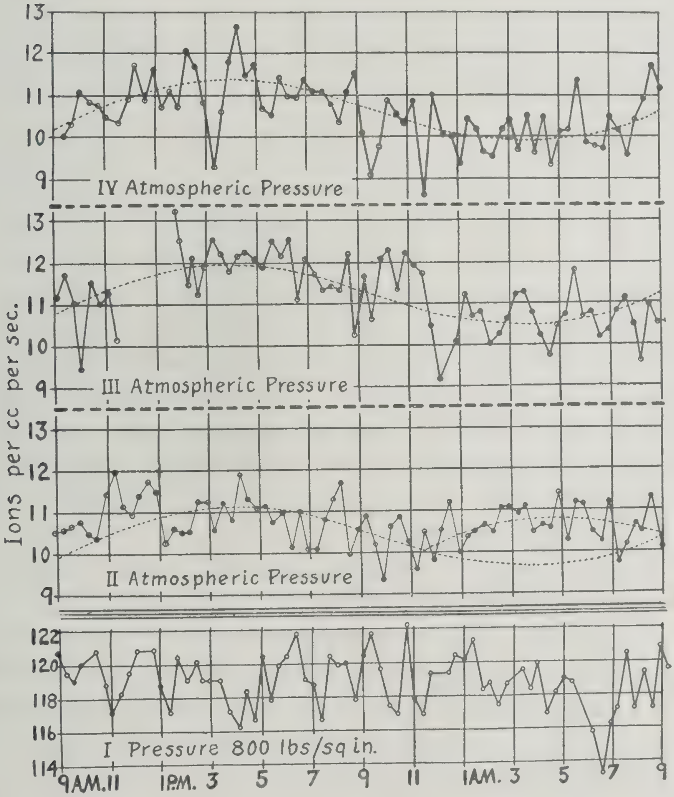

FIG. 6. Variation during 24-hr periods of the natural ionization in air at atmospheric pressure and at 800 lb./sq. in.

absolute values but the smaller fractional values of the variations occurring at the higher pressure may be explained in terms of fluctuations of soft radiations supposed to contribute to the total ionization.

INFLUENCE OF CHEMICAL ACTION

It has sometimes been suspected that chemical action might account for a part of the natural ionization in gases. With this possibility in mind, observations of the natural ionization occurring in air contained at atmospheric pressure in the 12 in. sphere were made before and after the admission of small quantities of hydrogen which would be expected to combine to a slight extent with the oxygen in the air. Also, observations of the natural ionization occurring within the 12 in. sphere in which had been placed pieces of silver foil and which had been filled with oxygen to atmospheric pressure were made before and after the admission of small quantities of hydrogen sulphide and also other quantities of silver.

In common with previous results,[20] those of the present investigation were negative so far as the detection of the dependence of the natural ionization in gases at atmospheric pressure upon slow chemical action is concerned. In certain cases there appeared to be slight increases in ionization at times coincident with increased chemical action. When the ionization values were plotted against the time, however, it was seen that there was practically no justification for the conclusion that the natural ionization was affected by the slow chemical action which resulted upon the admission of the different materials. That chemical action did occur upon admission of the hydrogen sulphide was evidenced by the tarnished condition of the silver and the brass parts of the apparatus subsequently observed.

In conclusion, the writer wishes to express his appreciation of the very general cooperation of the Physics faculty at Yale University where the experimental work was completed, and of the particularly kindly interest of Professor John Zeleny. Thanks are extended to Mr. C. J. Pietenpol who assisted in taking some of the readings, and to Professor W. B. Pietenpol for reading this paper. Finally, the writer desires to acknowledge his especial indebtedness to Professor W. F. G. Swann who suggested this research and who offered many helpful suggestions during the progress of the work.

HALE PHYSICAL LABORATORY,
UNIVERSITY OF COLORADO,
January 16, 1926.

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[20] K. H. Kingdon, Phil. Mag. **32**, 396 (1916).
N. R. Campbell, Phil. Mag. **9**, 545 (1905).

TRANSITION PROBABILITIES: THEIR RELATION TO THERMIONIC EMISSION AND THE PHOTO-ELECTRIC EFFECT

By Ernest O. Lawrence*

Abstract

Assuming (a) Wien's formula for black body radiation, (b) that electrons ejected thermally from a hot body have the experimentally known Maxwell distribution of velocities, and (c) that photo-electric emission from a solid surface is independent of the temperature of the solid, a theory is developed which leads directly to Richardson's thermionic current equation without importing into the argument circumstances not realized in experiment or assumptions and approximations that can be questioned. Detailed consideration of the mechanism of emission and absorption along the lines of Einstein's derivation of Planck's radiation formula leads to the same expression for the ratio of absorption to emission B_ν/q_ν obtained in other theories based on application of the principle of detailed balancing of processes occurring in systems in equilibrium. It is thus shown that observed photo-electric and thermionic phenomena from solid surfaces may be regarded as experimental confirmations of expressions B_ν/q_ν deduced in such theories.

AMONG the theories developed to account for thermionic phenomena are those which regard the emission of electrons from hot bodies as a photo-electric effect connected with the associated temperature radiation.[1] This view of the matter is in formal harmony with the ideas underlying Einstein's derivation of Planck's formula. Inasmuch as these theories, for example, Richardson's theory of the so-called "complete photo-electric emission," lead to an expression for the relative efficiencies of light of various frequencies in ejecting electrons from a metal surface, they are intimately related to more recent theories designed to evaluate transition probability coefficients, notably those of Kramers,[2] Milne[3] and Becker[4]. Richardson's theory was developed by statistical and thermodynamical considerations of a system of free electrons in equilibrium with an adjacent hot body and necessitated assumptions and approximations which were open to question, as indeed, the author of the theory indicated. In the present paper an attempt is made to deduce from experimentally recognized assumptions the probability of photo-electric emission from a solid surface as a function of the frequency of the light. The probability, so calculated, is then applied to a new derivation of the ratio of the probabilities of absorption and emission B_ν/q_ν, a ratio which has been obtained in the theories mentioned above by application of a principle of detailed balancing to a system in equilibrium.

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* National Research Fellow.

[1] Richardson, "Emission of Electricity from Hot Bodies," p. 110.

[2] Kramers, Phil. Mag. **46**, 836 (1923).

[3] Milne, Phil. Mag. **47**, 209 (1924).

[4] Becker, Zeits f. Physik **18**, 325 (1923).

It is our purpose to avoid the necessity of invoking circumstances not realized or assumptions that are not directly verified experimentally and we shall start with two universal properties of matter now well established. First, we have the spectral energy distribution I_ν of the radiation associated with the temperature T as represented by Wien's expression for high frequencies,

$$I_\nu=8\pi h\nu^3C^{-3}e^{-h\nu/kT} \tag{1}$$

and secondly the distribution of velocities of the electrons emitted thermally from a body at temperature T, viz.,

$$n_w=N(T)w^3e^{-mw^2/2kT}dw \tag{2}$$

where n_w is the number emitted per second with speeds in the range $w, w+dw$. It is to be noted that $N(T)$ is a function of T only and w comes in as a factor raised to the third power instead of squared because the number emitted per second is proportional to the velocity and the Maxwellian distribution. The fact that these two properties are common to all kinds of matter suggests a close relationship and we shall adopt the plausible hypothesis that the electrons are ejected photo-electrically by the temperature radiation. This hypothesis is in strict harmony with the viewpoints of the more recent theories mentioned above. Now the number of electrons n_ν ejected by radiation of frequencies between ν and $\nu+d\nu$ will be proportional to the intensity $I_\nu d\nu$ and the probability $f(\nu)$ of unit intensity ejecting an electron, that is,

$$N_\nu=f(\nu)I_\nu d\nu \tag{3}$$

This relation may be simply regarded as defining $f(\nu)$. Further, it is well known that the velocity of the photo-electrons w produced by radiation of frequency ν is given by,

$$\tfrac{1}{2}mw^2=h(\nu-\nu_0) \tag{4}$$

where ν_0 is the smallest frequency able to eject photo-electrons from the surface—the threshold frequency.

On the basis of our hypothesis it follows from (2) and (4) that the number emitted per second by frequencies $\nu, \nu+d\nu$ is

$$n_\nu=2N(T)(h/m)^2(\nu-\nu_0)e^{-h(\nu-\nu_0)/kT}d(\nu-\nu_0) \tag{5}$$

In view of (1) on equating (3) and (5) we have

$$f(\nu)=\frac{hc^3}{4\pi m^2}N(T)e^{h\nu_0/kT}\frac{(\nu-\nu_0)}{\nu^3} \tag{6}$$

Experiments have demonstrated that photo-electric effects are independent of the temperature of the radiated body so that this probability function is independent of the temperature. Because of the presence of the factor $e^{h\nu_0/kT}$ in the expression we deduce as a consequence thereof that

$$N(T)=\alpha e^{-h\nu_0/kT} \tag{7}$$

where α is a constant.

Thus we conclude that the magnitude of the photo-electric emission from a solid surface when illuminated by unit intensity of frequency ν is

$$f(\nu)=\frac{\alpha hc^3}{4\pi m^2}\frac{(\nu-\nu_0)}{\nu^3}$$

That this is the correct law of variation of the photo-electric effect from solid surfaces has been verified in several instances. Richardson obtained a similar expression and the experiments of K. T. Compton and Richardson[5] were the first to show that, as the formula predicts, light of frequency 3/2 of the threshold value is the most efficient in the production of a photo-electric effect. Later Souder[6] obtained confirmative data of possibly greater precision. Finally should be mentioned the experiments of Wilson[7] who observed the variation of the photo-electric effect from a sodium surface when illuminated by radiation from a black body at various temperatures. As will be seen below, this probability function implies that the photo-electric currents thus observed should vary with the temperature of the black body according to Richardson's thermionic equation. Wilson's experiments confirmed this implication.

The total thermionic current i may be deduced readily as a function of the temperature and threshold frequency, for clearly it is,

$$i=\int_0^\infty N_w\epsilon\ dw$$

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[5] K. T. Compton and O. W. Richardson, Phil. Mag. **26,** 549 (1913).

[6] Souder, Phys. Rev. **8,** 310 (1916).

[7] Wilson, Proc. Roy. Soc. **A93,** 359 (1917).

From (2) and (7) we have, therefore,

$$i=\epsilon\alpha e^{-h\nu_0/kT}\int_0^\infty w^3 e^{-mw^2/2kT}dw$$

$$=AT^2e^{-b/T}, \qquad b=h\nu_0/k$$

which is Richardson's thermionic equation. Thus we have correlated the facts of thermionics and the photo-electric effect without invoking a system in thermodynamic equilibrium and, except for the hypothesis that thermionic emission is a photo-electric effect, our assumptions are experimental facts.

Now Milne obtains from thermovdnamical considerations and the principle of detailed balancing* the ratio B_ν/q_ν for optical frequencies, where B_ν is the probability that an electron in the normal energy level will be raised to a higher energy state when in the presence of unit light intensity of frequency ν and q_ν is the effective collision-capture area of an atom capable of capturing an electron in the higher state, thereby reducing it to its normal condition.

The significance of the probability function $f(\nu)$ as defined above is quite distinct from that of the transition probability coefficient B_ν of Milne's theory for, clearly, $f(\nu)$ is proportional to the probability that an electron will be raised from a given stationary state to one of higher energy and, before recombining, escape from the surface. However, having ascertained $f(\nu)$ we are able to deduce the ratio B_ν/q_ν. The following analysis makes this clear.

Consider an annular volume element $d\tau$ of a metal relative to an element dA of its surface, i. e.,

$$d\tau=2\pi r^2 \sin\theta \, d\theta \, dr$$

where r is the distance of any portion of $d\tau$ from dA. The number of electrons raised from the normal state to a free state of higher energy per unit time in $d\tau$ by absorption of light of frequency ν, $\nu+d\nu$ and intensity $I_\nu d\nu$ is, according to Milne's theory,

$$N\, d\tau B_\nu I_\nu d\nu$$

where N is the number of electrons in the normal configuration per unit volume. Of this number there will be a portion $dA\cos\theta/4\pi r^2$ which have velocities such as to cause them to pass through the element of surface dA if they are not absorbed in their passage thereto. But we further recognize that of the number in the higher state there will always be a certain portion dn that will be absorbed again in time dt, i. e.,

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* It may be remarked parenthetically that the principle of detailed balancing is simply that in a system in equilibrium the number of elementary processes occurring in a forward direction in unit time is equal to the number in the reverse direction.

$$-dn=A_\nu n\,dt$$

where $-dn$ is the number absorbed of a group n in time dt. Thus integrating we have,

$$n=n_0e^{-A_\nu t}$$

where n is the number unabsorbed after a time t of a group n_0 existing at $t=0$. Clearly the time taken for an electron to pass from the annular volume element $d\tau$ to the surface element is

$$t=r/w$$

In view of these considerations we have that the total number reaching dA per unit time which have been raised from the normal state to the higher energy value by radiation of frequency $\nu,\nu+d\nu$ is

$$i_\nu dA=\frac{1}{2}NdAB_\nu I_\nu d\nu\int_0^{\pi/2}d\theta\int_0^\infty dr\sin\theta\cos\theta\, e^{-A_\nu r/w}$$

which reduces to

$$i_\nu=\frac{1}{2}NI_\nu d\nu\frac{w}{A_\nu}B_\nu \tag{8}$$

Now we have shown that the magnitude of the emission from a surface by light of frequency ν, $\nu+d\nu$ and intensity $I_\nu d\nu$ is

$$i_\nu=\frac{\nu-\nu_0}{\nu^3}I_\nu d\nu\times\text{constant} \tag{9}$$

From (8) and (9) therefore we have that

$$\frac{w}{A_\nu}B_\nu=\frac{\nu-\nu_0}{\nu^3}\times\text{constant}$$

which may be written in the form

$$\frac{B_\nu}{q_\nu}=\frac{\nu-\nu_0}{\nu^3}\times\text{constant}$$

where

$$q_\nu=\frac{A_\nu}{w}\times\text{constant}$$

is the effective "collision-capture area" of an atom relative to a ν-electron.

Thus by a procedure quite distinct from the method of detailed balancing of the processes occurring in a system in complete equilibrium we have obtained the ratio of absorption to emission, B_ν/q_ν.

In this connection it should be emphasized that the probability of absorption A_ν and the effective collision area q_ν do not refer to a process involving the return of the electron to the normal state in the atom but to any state that prevents its escape from the surface. In Milne's theory the effective collision area concerns the capture of an electron wherein it is returned to the same stationary state from which it was ejected by the light of frequency ν. The similarity of the present expression B_ν/q_ν with the analagous ratios in theories based on the principle of detailed balancing suggests that the probability of capture and return to a state other than the normal one is the same function of the frequency as, or negligible in comparison to, the probability of return to the normal state. Of course we have implicitly regarded elastic impacts of the electrons with atoms as of no importance in the calculations.

Having obtained the ratio of the probabilities of absorption B_ν and emission q_ν various attempts have been made to evaluate the absorption probability B_ν by determining the nature of the emission q_ν with the ultimate end in view of a comparison with experiment. In the optical region the outstanding experiments on such absorption probabilities are the very interesting experiments of Foote, Mohler and Chenault[8] on the photo ionization of caesium vapor and also there is Lawrence's[9] observation of the variation with the frequency of the photo-electric effect in rapidly distilling potassium vapor. The absorption in caesium vapor was observed to decrease rapidly from the series limit to higher frequencies in a manner not in accord with any theoretically determined B_ν, while the experiments with the jet of potassium vapor revealed that the absorption increased from a threshold value ν_0 to higher frequencies over the range investigated according to the law*

$$B_\nu' = \frac{(\nu-\nu_0)^{3/2}}{\nu^3} \times \text{constant}$$

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[8] Mohler, Foote and Chenault, Phys. Rev. **27,** 37 (1926).

[9] Lawrence, Phil. Mag. **50,** 345 (1925).

* This law was deduced from the data of Fig. 3 (above reference) assuming that the potassium photo-cell used to measure relative light intensities was selective according to the function $f(\nu)$ deduced in the present paper.

a variation with frequency also in disaccord with all theoretically evaluated expressions for B_ν. Now, therefore, it is interesting to point out that, on the basis of the deductions herein given, *thermionic and photo-electric phenomena observed from solid surfaces may be regarded as experimental confirmations of the ratio* B_ν/q_ν *evaluated in statistical equilibrium theories.*

It is an especial pleasure to acknowledge my indebtedness to Professor W. F. G. Swann and Professor Leigh Page.

SLOANE LABORATORY,
YALE UNIVERSITY,
February 17, 1926.

MAY, 1926 PHYSICAL REVIEW VOLUME 27

THE ABSORTION SPECTRA OF TELLURIUM, BISMUTH, CHROMIUM AND COPPER VAPORS IN THE VISIBLE AND ULTRAVIOLET

By R. V. Zumstein

Abstract

Using a hot carbon tube at about 1600°C as the absorption cell, the spectra of these elements have been studied in absorption from 6000 to 2000A. The vapor of tellurium was dissociated into atoms by a simple device and 4 absorption lines were found. Two new arc lines were measured. The same arrangement gave 8 bismuth absorption lines, 4 being new. These are exactly the lines to be expected from the work of Ruark, Foote, Mohler and Chenault. Four new arc lines were measured in the spectrum of a 75 ampere arc. Chromium was placed directly in the carbon tube and 3 triplets were absorbed. Nineteen copper lines were absorbed, 10 being from the normal state in agreement with Shenstone and McLennan and McLay and 9 new ones from excited states.

THE absorption spectrum of tellurium vapor was investigated by Evans[1] at various pressures and temperatures. He found that if a small quantity of tellurium was gradually heated in an enclosed quartz tube, the vapor was opaque or showed absorption bands. As the vapor was heated, it became more transparent and the bands disappeared. At a temperature of about 1000°C and a sufficiently low pressure, the vapor was perfectly transparent from the visible to 2500A. His interpretation was that at low temperatures and high vapor pressures the molecules of tellurium vapor are composed of several atoms and that at high temperatures these molecules dissociate into atoms if the pressure is low so that there is slight chance of recombination.

Guided by Evans' experiments, I have modified the method used for manganese.[2] The tellurium was not placed directly in the carbon tube but in a small iron tube as shown in Fig. 1. C is the carbon tube heated by the torch T. The hottest part of the tube was at about 1600°C and the coldest at 800°C. Te is the tellurium in the small iron tube at about 500°C. Through a second tube N, a gentle stream of nitrogen flowed to displace the atmospheric oxygen from the tube. By this method four absorption lines were observed corresponding to the arc lines 2385.793, 2383.268, 2259.02 and 2142.94. The first pair were sharp absorption lines but the last two were quite broad.

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[1] Evans, Astrophys. J. **36,** 228 (1912).

[2] Zumstein, Phys. Rev. **26,** 765 (1925).

The tellurium arc for comparison was obtained by placing tellurium in the lower carbon of a 50 ampere arc. The spectrum so obtained was similar to that described by Uhler and Patterson.[3] To their list of 15 arc lines I would add a strong pair of reversed lines at 2001.87 and 1994.07. Their lines 2208.58, 2160.1 were observed as diffuse reversals and 2147.33, 2081.8 as sharp reversals. I have not been able to make any analysis of the tellurium arc spectrum beyond a guess that the lowest lying levels are rather widely separated *p* levels which would combine with *s* and *d* levels to give the sharp and diffuse lines observed in the arc spectrum. McLennan, Smith and Peters[4] have recently observed a group of tellurium arc lines in the near infrared.

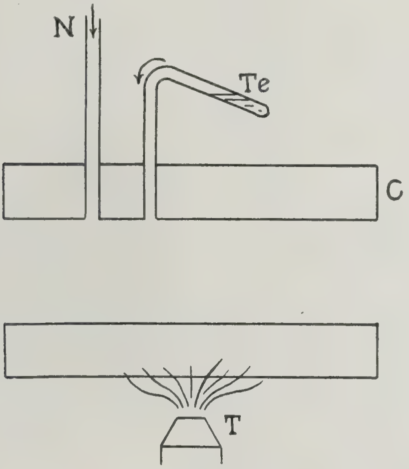

FIG. 1

Bismuth. Since some of the bismuth absorption lines appeared while studying the absorption spectrum of tellurium vapor, it seemed worth while to repeat the experiments with pure bismuth using the arrangement of Fig. 1. The 8 absorption lines observed are given in Table I. The first four of these lines were observed in absorption by Ruark, Mohler, Foote and Chenault.[5] They state that a band absorption extended from 2205A to the shorter wave-lengths. It may be that these bands were due to bismuth molecules which were dissociated in the present experiments. All of the absorptions are from the state called $3d_2$ by Ruark, etc., and afford very good support of the analysis of the bismuth arc spectrum which they give.

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[3] Uhler and Patterson, Am. Journal of Science **186,** 135 (1913).

[4] McLennan, Smith and Peters, Trans. Roy. Soc. Canada, III, **39** (1925).

[5] Ruark, Mohler, Foote and Chenault, B. S. Sci. Papers, **19,** 484 (1924).

A bismuth arc of 70 amperes gives an intense continuous spectrum extending from the visible to 1900A with the bismuth arc lines reversed. I have compared this arc with that given by Ruark, etc. between 2075 and 2000A. Their lines 2020.5, 2068.99 and 2073.2 were not observed and are perhaps not arc lines. Four new lines were found namely: 2064.4 (2*R*), 2057.4 (2*R*), 2041.8 (2*R*) and 2041.6 (2*R*). The difference in frequency of 2041.8 (48960) and 2582.1 (38718) equals $3d_1^B - 3D_1^A$. Also the frequency difference of 2041.6 (48964) and 2224.2 (44946) equals $3d_1^B - 3D_2$. This enables us to classify these four bismuth lines and to evaluate two terms 2490 and 2486 which resemble several other bismuth terms in being a close pair. A classification of the bismuth arc spectrum has also been given by Kopferman[6] who indicates that 2582.1 comes from $3d_1^B$ which cannot be correct as it is not reversed and also from $3D_2$ which is possible.

TABLE I

Bismuth absorption spectrum

λ(I.A.)	Intensity 70 amp. arc	 Absorption	Series notation
3067.732	10R	10	$3d_2-\alpha$
2276.578	6R	5	$3d_2-\delta$
2230.626	10R	10	$3d_2-\epsilon$
2228.240	8R	9	$3d_2-\zeta$
2177.33*	3R	2	$3d_2-\eta$
2110.263*	8R	6	$3d_2-\theta$
2061.73*	10R	9	$3d_2-\iota$
2020.99*	3R	2	$3d_2-\kappa$

* New absorption lines

Chromium. The absorption spectra of chromium and copper vapors were investigated by placing a piece of the metal in the carbon tube and heating it directly to about 1600°C. The method was the same as that used for manganese.[2] Three chromium triplets were observed in absorption as shown in Table II. The first two triplets had been previously observed in absorption by Grotrian and Gieseler[7] and by McLennan and McLay.[8] In fact these nine lines and many others were obtained in the chromium absorption spectrum by King[9]. In King's experiments, the vapor was at only one temperature, 2600°C. He obtained absorptions from the normal state and from some of the excited states. It is not therefore obvious from his results that the triplet 2366, 2365, 2364 are transitions to the normal state which does follow from the present experiments. The threefold ^7p term defined by this triplet should combine with the 5^7s term (see Gieseler's article on the arc spectrum of chromium[10]) to give a triplet in the infrared of wave-lengths 18716, 18661, 18585A. Randall and Barker[11] found a chromium triplet at 18717.0 ($I=20$), 18654.2 (30), 18583.5 (30). The agreement appears to be satisfactory.

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[6] H. Kopfermann, Zeits. f. Physik **21,** 322 (1924).

[7] W. Grotrian and H. Gieseler, Zeits. f. Physik **22,** 245 (1924).

[8] McLennan and McLay, Trans. Roy. Sco. Canada, **III,** 89 (1925).

[9] A. S. King, Astrophys. J. **60,** 291 (1924).

TABLE II

Chromium absorption spectrum

λ(I.A.)	ν	Series
4289.726	23304.98	4^7s-4^7p
74.802	386.34	
54.341	498.81	
3605.330	27728.83	4^7s-4^7p
593.483	820.24	
78.688	935.25	
2366.85	42237.5	4^7s-5^7p
65.96	53.3	
64.74	75.1	

Copper. It seemed desirable to repeat my former experiments on the absorption of copper vapor,[12] using the large Hilger spectroscope, size E_1, which is now available. Shenstone,[13] McLennan and McLay,[8] and Stücklen[14] have recently studied this problem. Shenstone gives evidence for a pair of metastable states (one is the X term introduced by Randall[15]) which are not far removed from the normal state ($\Delta\nu=$ 13245.4 and 11202.5).

With the copper vapor at about 1200°C, I obtain a series of absorption lines which appear to come from copper atoms in the normal state. When the temperature is increased to 1600°C, most of these lines increase in width and a group of faint absorption lines appear which I think are due to copper atoms in excited states. These two groups are given in Table III.

All of the absorption lines from the normal state were obtained by Shenstone and by McLennan and McLay. The three lines 2492, 2441 and 2244 were narrow absorption lines at the highest temperature. The remainder from the normal state widen out with increase of temperature. All of the absorption lines from the metastable states were sharp. The narrow pair, 2199.73 and 2199.57 were observed as two reversals in the arc as noted by Shenstone and Stücklen. They were absorbed as two narrow absorption lines by the vapor. At high temperatures a group of absorption bands appeared from 2275 to 2228A as found by Stücklen in the copper spark under water. Because of these bands, one cannot be certain if there was faint absorption at some of the arc lines in this region. By changing the inductance and capacity of the circuit of the under water spark, Stücklen obtained a group of copper arc lines which were considered to come from the normal state. The grouping so obtained is considerably different from that afforded by the more direct method of heating the vapor in a tube with a torch.

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[10] H. Gieseler, Zeits. f. Physik **22,** 243 (1924).

[11] Randall and Barker, Astrophys. J. **49,** 58 (1919).

[12] Zumstein, Phys. Rev. **25,** 523 (1925).

[13] Shenstone, Phil. Mag. **49,** 952 (1925).

[14] Stücklen, Zeits. f. Physik **33,** 562 (1925).

[15] Randall, Astrophys. J. **34,** 1 (1911).

TABLE III

Copper absorption spectrum

Wave-lengths from normal state	Wave-lengths from excited state
3273.976	5105.551*
3247.550	2392.629* very faint
2492.142 sharp	2293.832*
2441.625 sharp	2230.071*
2244.240 sharp	2227.74*
2225.665	2215.65* very faint
2181.68	2214.56*
2179.91	2199.73*
2165.06	2199.57*
2024.3	

* New absorption lines

The present experiments show very clearly that the copper atom has one or more metastable states which differ in frequency from the normal state by about 10,000 cm^{-1}. They do not show the exact value of this difference. In the copper arc spectrum, there are pairs in the visible and near ultraviolet having the frequency difference of 248.4, which is that of the two lines 3274 and 3247. If any of these pairs should show the faint absorption corresponding to the metastable states, then we can evaluate with certainty the terms which correspond to the metastable states. According to Shenstone's work, we should expect that the green line 5105 would be absorbed and at slightly higher temperature the yellow pair 5782. and 5700. I have frequently studied the copper absorption in the visible but always with negative results. Recently we have received from A. Hilger and Co. a glass prism and lens to fit their E_1 quartz spectrograph. Having available therefore a dispersion of 12A per mm at 5700 A, I have returned to the problem and find that in the visible spectrum only the green line 5105 is faintly absorbed at the highest temperatures. The fact that the yellow pair was not absorbed is not an argument against Shenstone's work because the absorption of the green line 5105 was only observed on a small fraction of the plates taken. To obtain the yellow pair in absorption would require a still higher temperature.

National Research Fellowship,
Physics Department,
University of Michigan,
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MAY, 1926 PHYSICAL REVIEW VOLUME 27

THE QUANTUM THEORY OF THE DIELECTRIC CONSTANT OF HYDROGEN CHLORIDE AND SIMILAR GASES

BY LINUS PAULING*

ABSTRACT

The quantum theory of diatomic dipoles.—Using the treatment of Pauli, an expression for the dielectric constant of a diatomic dipole gas is obtained, in which half-quantum numbers are used. It is shown that for cases of practical interest the approximation suggested by Pauli is not valid; hence numerical values of the temperature-function C have been calculated and tabulated.

Application to experimental measurements.—The theory has been applied in the interpretation of Zahn's measurements of the dielectric constants of the hydrogen halides. The electric moments of molecules of hydrogen chloride, bromide, and iodide were found to be 0.3316, 0.252, and 0.146×10^{-18} cgsu respectively; i.e., only about one-third of the values given on the basis of the classical theory. Moreover, the values 0.00077 and 0.00102 for $4\pi N_0\alpha$ for hydrogen chloride and bromide, in which α is the coefficient of induced polarization, are shown to be in better agreement with measurements of indices of refraction than are the classical theory values. A discussion is given of possible inaccuracies in the theory, of the choice of quantum numbers, and of the possibility of weak quantization.

INTRODUCTION

UNDER the influence of an electric field a gas whose molecules have a permanent electric moment and in addition can have a further moment induced in them by deformation becomes polarized in the direction of the field, the amount of polarization per unit volume being[1]

$$P=\frac{3}{4\pi}\,\frac{\epsilon-1}{\epsilon+2}F=N\mu\,\overline{\overline{\cos}}\,\theta+N\alpha F\ , \tag{1}$$

in which ϵ is the dielectric constant of the gas, F the strength of the applied field, N the number of molecules in unit volume, μ the permanent electric moment of a molecule, and α the coefficient of induced polarization of a molecule. $\overline{\overline{\cos}}\theta$ is the average value of $\overline{\cos}\,\theta$ for all molecules in the gas, and $\overline{\cos}\theta$ is the time-average of $\cos\theta$ for one molecule in a given state of motion, θ being the angle between the axis of the electric dipole and the lines of force of the applied field.

An expression for $\overline{\overline{\cos}}\theta$ applicable to polyatomic molecules in general was obtained by Debye[2] with the use of classical statistical mechanics.

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* National Research Fellow in Chemistry.

[1] See, for example, Debye in Marx "Handbuch der Radiologie," Leipzig Akademische Verlagsgesellschaft, 6, 619 (1925).

[2] P. Debye, Phys. Zeits. 13, 97 (1912).

From the Maxwell-Boltzmann distribution law the probability that the axis of the electric dipole in the molecule will lie between the angles θ and $\theta+d\theta$ with the lines of force is

$$\frac{e^{\mu F\cos\theta/kT}\sin\theta\,d\theta}{\int_0^\pi e^{\mu F\cos\theta/kT}\sin\theta\,d\theta},$$

and the average value of $\cos\theta$ is

$$\overline{\overline{\cos\theta}}=\frac{\int_0^\pi e^{\mu F\cos\theta/kT}\cos\theta\sin\theta\,d\theta}{\int_0^\pi e^{\mu F\cos\theta/kT}\sin\theta\,d\theta}. \tag{2}$$

This expression becomes on integration the Langevin function,

$$L\left(\frac{\mu F}{kT}\right)=\coth\frac{\mu F}{kT}-\frac{kT}{\mu F},$$

which reduces for values of μF small in comparison with kT to

$$\overline{\overline{\cos\theta}}=\frac{1}{3}\,\frac{\mu F}{kT}. \tag{3}$$

This result must now, however, be replaced by one based upon the quantum theory. In this case a generally applicable expression cannot be obtained, and it is necessary to consider particular molecular models. The simplest of these, the diatomic molecule for which the axis of the electric dipole coincides with the line joining the nuclei of the two atoms, is believed to represent the hydrogen halides, for which data are available to make possible the evaluation of their electric moments.

THE QUANTUM THEORY OF THE DIATOMIC DIPOLE

The dielectric constant of diatomic dipole gases has been treated on the basis of the quantum theory by W. Pauli, Jr.,[3] whose treatment forms the basis of the following discussion.

The Hamiltonian function for the motion of a diatomic dipole in an electric field, using polar coordinates with the polar axis in the direction of the lines of force, is

$$H=\frac{1}{2I}\left(p_{\theta^2}+\frac{p_\varphi^2}{\sin^2\theta}\right)-\mu F\cos\theta, \tag{4}$$

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[3] W. Pauli, Jr., Zeits. f. Physik **6**, 319 (1921).

in which p_θ and p_ϕ are the momenta corresponding to the coordinates θ and φ, and I is the moment of inertia of the rotator about an axis through its center of mass and normal to the lines joining the atomic nuclei. The coordinate φ is cyclic, and p_ϕ is accordingly constant. Applying the Wilson-Sommerfeld quantum conditions we write

$$\oint p_\theta d\theta + \left| \oint p_\varphi \, d\varphi \right| = mh \tag{5}$$

and

$$\oint p_\varphi \, d\varphi = 2\pi p_\varphi = nh, \tag{6}$$

in which m and n are the two quantum numbers describing the condition of motion of the rotator. Introducing (6) and the relation $p_\theta = I\dot{\theta}$ in (4), there is obtained the differential equation

$$dt = \frac{2\pi I \, d\theta}{\sqrt{8\pi^2 IW - \dfrac{n^2h^2}{\sin^2\theta} + 8\pi^2 I\mu F \cos\theta}}, \tag{7}$$

in which W is the energy-constant. The time-average value of $\cos\theta$ for a rotator in a given state of motion is, then,

$$\overline{\cos\theta} = \frac{\displaystyle\oint \left(8\pi^2 IW - \frac{n^2h^2}{\sin^2\theta} + 8\pi^2 I\mu F \cos\theta\right)^{-\frac{1}{2}} \cos\theta \, d\theta}{\displaystyle\oint \left(8\pi^2 IW - \frac{n^2h^2}{\sin^2\theta} + 8\pi^2 I\mu F \cos\theta\right)^{-\frac{1}{2}} d\theta}. \tag{8}$$

If μF is very small in comparison with the total energy W these expressions may be expanded in powers of μF and terms higher than linear neglected; it is, moreover, permissible to substitute for W the value $W_0 = m^2h^2/8\pi^2 I$ corresponding to zero field. Upon evaluating the resultant integrals by contour integration there is obtained the expression

$$\overline{\cos\theta} = \frac{4\pi^2\mu F I}{m^2h^2}\left(\frac{3}{2}\,\frac{n^2}{m^2} - \frac{1}{2}\right). \tag{9}$$

Pauli assigned to m values 1, 2, 3, $\cdots\cdots \infty$, and to n ± 1, ± 2, ± 3, $\cdots\cdots$ $\pm m$. We shall give m the values 1/2, 3/2, 5/2, $\cdots\cdots \infty$, and n $\pm 1/2$, $\pm 3/2$, $\pm 5/2$, $\cdots\cdots$ $\pm m$; for these half-quantum numbers for m are indicated by the infra-red oscillation-rotation absorption spectrum[4] of hydrogen chloride and definitely required by the recently observed[5] pure rotation absorption spectrum. The choice of values for n will be discussed later. Assigning equal *a priori* probabilities to all of the possible quantum states characterized by half-integral values of m and n we have for the probability of a given state

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[4] Colby, Astrophys. J. 58, 303 (1923).

$$\omega(m,n)=\frac{e^{-W/kT}}{\sum\limits_{m=\frac{1}{2}}^{\infty}\sum\limits_{n=-m}^{+m}e^{-W/kT}}\,. \tag{10}$$

Introducing the variable $\sigma=\Theta/T=h^2/8\pi^2IkT$ we obtain the following expression for $\overline{\overline{\cos\theta}}$:

$$\overline{\overline{\cos\theta}}=\frac{\mu F}{kT}\,\frac{1}{2\sigma}\,\frac{\sum\limits_{m=\frac{1}{2}}^{\infty}\sum\limits_{n=-m}^{+m}\frac{1}{m^2}\left(\frac{3}{2}\,\frac{n^2}{m^2}-\frac{1}{2}\right)e^{-\sigma m^2}}{\sum\limits_{m=\frac{1}{2}}^{\infty}\sum\limits_{n=-m}^{m}e^{-\sigma m^2}}\,. \tag{11}$$

Pauli, who obtained a similar expression with whole quantum numbers, evaluated the sums by assuming σ to be very small. This is not justifiable, however, for it leads to results in error by 30 percent or more in cases of practical interest, for which σ has values near 0.05. Replacing m by $r-\frac{1}{2}$ and n by $s-\frac{1}{2}$ and summing for s one obtains

$$\overline{\overline{\cos\theta}}=\frac{\mu F}{kT}C\,, \tag{12}$$

where

$$C=\frac{1}{4\sigma}\,\frac{\sum\limits_{r=1}^{\infty}\frac{r}{(r-\frac{1}{2})^3}e^{-\sigma(r-\frac{1}{2})^2}}{\sum\limits_{r=1}^{\infty}re^{-\sigma(r-\frac{1}{2})^2}}\,. \tag{13}$$

For very large values of σ; i. e., for very low temperatures, C is equal to $2/\sigma$. As σ tends to zero C approaches asymptotically the value 4.570, for $\sum\limits_{r=1}^{\infty}\frac{r}{(r-\frac{1}{2})^3}e^{-\ (r-\frac{1}{2})^2}$ approaches $\sum\limits_{r=1}^{\infty}\frac{r}{(r-\frac{1}{2})^3}$, which has the value 9.140, and $\sum\limits_{r=1}^{\infty}re^{-\sigma(r-\frac{1}{2})^2}$ can be replaced by the integral $\int_0^{\infty}re^{-\sigma(r-\frac{1}{2})^2}\,dr$, which is equal to $1/2\sigma$. C has been determined for intermediate values of σ by numerical substitution, from five to twenty-five terms being used in order that the final figure might be accurate to 0.05 percent. The results of the calculations are given in Table I.

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[5] **Czerny, Zeits. f. Physik 34, 227 (1925).**

TABLE I

σ	C	σ	C
Very large	$2/\sigma$	0.05	3.599
1.00	1.578	.04	3.690
0.20	2.848	.03	3.796
.10	3.264	.02	3.929
.07	3.445	0.00	4.570

CONSIDERATION OF EXPERIMENTAL RESULTS

Substituting (12) in (1), we obtain

$$\frac{3}{4\pi}\,\frac{\epsilon-1}{\epsilon+2}=N\frac{\mu^2}{kT}C+N\alpha\ , \tag{14}$$

in which C is a function of the temperature. This property differentiates this result from those of Debye and Pauli, who obtained for C the constant values 1/3 and 1.5367 respectively. Since for gases $\epsilon+2$ is approximately 3, we may write

$$(\epsilon-1)T=4\pi N\frac{\mu^2}{k}C+4\pi N\alpha T\ . \tag{15}$$

The equations of Debye and Pauli require that a plot of $(\epsilon-1)_0T$, in which the subscript 0 indicates that the dielectric constant is that of the gas at constant density (that at standard conditions), against T be a straight line; the calculations given in this paper, on the other hand, require the curve to deviate from a straight line, since C is found not to be a linear function of the temperature. Moreover, α and $4\pi N\alpha$ will have one value when obtained from measurements of ϵ with the use of the equation of Debye or of Pauli, and a different value if our calculations are used.

The only extensive measurements of the dielectric constants of diatomic dipole gases are those of Zahn[6] on hydrogen chloride, bromide, and iodide. Values of Θ for these gases are obtained in the interpretation of their infra-red spectra. Czerny[5] gives for hydrogen chloride the value 10.397 for $hc/8\pi^2I$, which leads to $\Theta=14.9°$ for this gas. An equally accurate value for hydrogen bromide is not at hand, for its pure rotation spectrum has not been observed. Kratzer[7] gives for I the value 3.258×10^{-40} g. cm^2, from oscillation-rotation spectra, corresponding to $\Theta 12.15°$. Since Kratzer's value $I=2.594\times10^{-40}$g.cm^2 for hydrogen chloride corresponds to $\Theta=15.09°$, which is slightly high,

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[6] Zahn, Phys. Rev. **24,** 400 (1924).

[7] Kratzer, Zeits. f. Physik **3,** 289 (1920).

I have used for hydrogen bromide the value $\Theta = 12.0°$. No spectral data for hydrogen iodide have been obtained; from a consideration of atomic sizes obtained from crystal structure data I have predicted the approximate figures $I = 4.29 \times 10^{-40}$ g. cm^2 and $\Theta = 9.2°$ for this gas.

There are, then, two constants, μ and α, to be evaluated from the experimental data for each gas. These were determined in such a way as to cause the theoretical curve to pass through two experimental points, one at about 300° and one at about 500°A. The curves shown in Fig. 1 are obtained by placing $\mu = 0.3316 \times 10^{-18}$cgsu and $4\pi N_0\alpha = 0.00077$ for hydrogen chloride, and $\mu = 0.252 \times 10^{-18}$ and $4\pi N_0\alpha = 0.00102$ for hydrogen bromide; N_0 here represents the number of molecules per cc for the gas at standard conditions.

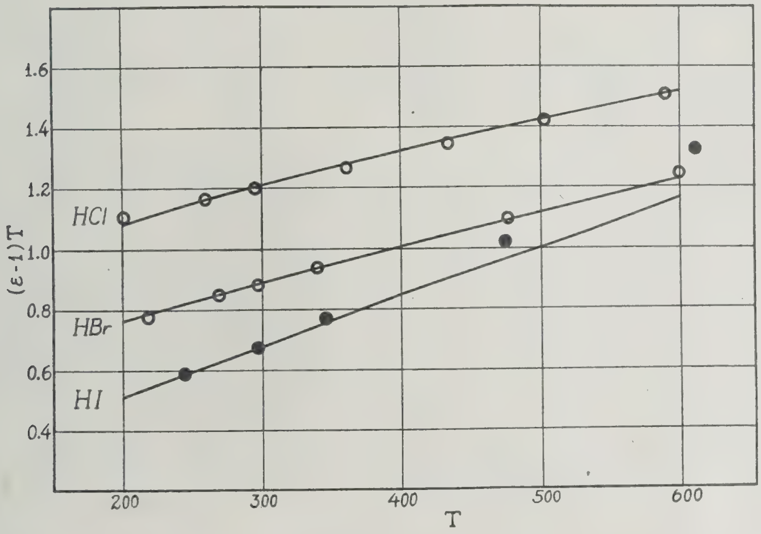

Fig. 1. Variation of $(\epsilon - 1)$T with T.

The interpretation of the data for hydrogen iodide is made difficult by the dissociation of the gas into its elements. It is desirable to obtain some information regarding the electric moment of these molecules, however, and so a different procedure has been followed. At the lowest temperature used, 244.5°A, Zahn obtained the value 0.5885 for $(\epsilon - 1)_0 T$, a value which can be accepted as correct, for the dissociation of hydrogen iodide is at that temperature only 1.3 percent. If the value 0.00160, obtained from optical data and discussed in the next section of this paper, be accepted as correct for $4\pi N_0\alpha$, then the value 0.146×10^{-18} cgsu for μ is required in order that the theoretical curve (shown in Fig. 1) might pass through this experimental point.

DISCUSSION OF RESULTS

The electric moments of the hydrogen halides. The values found for the electric moment μ of these gases are given in Table II, together with the classical theory values given by Zahn. It is to be noticed that the classical moments are not approximately equal to those obtained from the quantum theory, but are much larger—about three times as large. In these cases, then, considerations regarding, for example, molecular structure based on the classical values of the electric moments must be revised,[8] as has already been pointed out by Pauli[3] and by Ebert.[9] Indeed, it is probable that in the case of polyatomic molecules also the classical values of the electric moments may be considerably in error.

TABLE II

	μ		d	
	Quantum	Classical	Quantum	Classical
HCl	0.3316×10^{-18}	1.034×10^{-18}	0.0694 A.	0.217 A.
HBr	.252	0.788	.0528	.165
HI	.146	.382	.0306	.080

Under d in Table II is given the distance between an electron and a proton in order that the configuration might have the electric moment found for each of the hydrogen halides.

Their coefficients of induced polarization. In Table III are given the values found for $4\pi N_0\alpha$ for hydrogen chloride and bromide, and those given by Zahn with the use of the classical theory. The quantum theory values are confirmed by independent evidence; for they agree with Maxwell's relation $4\pi N_0\alpha = n_0^2 - 1$, in which n_0 is the index of refraction of the gas at standard conditions for light of frequency far from any frequency characteristic of the molecule. It is known that n determined with ordinary light is larger than n_0; hence the observed values of n^2-1 for the sodium D lines, given in Table III, cannot be reconciled with the considerably larger classical theory values of $4\pi N_0\alpha$, but support the quantum theory values.

TABLE III

	$4\pi N_0\alpha$		n^2-1 (sodium D lines)
	Quantum	Classical	
HCl	0.00077	0.001040	0.000888
HBr	.00102	.001212	.001140
HI	(.00160)	.001856	.001812

It will be seen that the values found for $4\pi N_0\alpha$ for hydrogen chloride and bromide are in each case about 88 percent of those for n^2-1 for the sodium D lines. For this reason it has seemed probable that $4\pi N_0\alpha$ for hydrogen iodide can be taken to be 0.00160, which is 88 percent of n^2-1 for this gas.

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[8] See, for example, Smyth, Jour. Amer. Chem. Soc. **46,** 2151 (1925); Phil. Mag. **47,** 530 (1924).

[9] Ebert, Zeits. f. Phys. Chem. **114,** 429 (1925).

The discrepancies between the theoretical curve and the experimental points. The experimentally found points for hydrogen chloride and bromide cannot be made to fall exactly on a curve of the type required by the quantum theory considerations of this paper. It is possible that experimental errors are responsible for this disagreement; further experiments are accordingly desired. On the other hand, the theoretical treatment has perhaps been over-simplified. The assumption that μF is much smaller than W is valid; thus for hydrogen chloride with fields of 10,000 volts/cm μF is less than 1×10^{-17} ergs, while W for the lowest quantum state ($m=\frac{1}{2}$) is over 50×10^{-17} ergs. We have further assumed the molecule to have a definite electric moment μ, independent of its state of rotation. That this assumption also is valid has been shown in the following way. The force tending to restore the proton to its equilibrium position when it is pulled away from the chlorine nucleus can be determined from oscillation-rotation spectra.[7] Equating this with the centrifugal force acting when the molecule is in rotation, it is possible to find the change in position of the nucleus on going from one state to another. The electric moment of hydrogen chloride is only about 6 percent of that which would be caused by a single negative charge located on the chlorine nucleus and a single positive charge on the proton; it seems reasonable then that an upper limit for the change in moment occurring on moving the proton in the molecule would be given by the product of the unit charge and the distance moved. On carrying out this calculation it is found that the possible changes in the electric moment are far too small to be of any influence on the dielectric constant.

The small lack of agreement between experiment and theory accordingly remains unexplained.

The choice of quantum numbers. The pure rotation spectrum of hydrogen chloride in the far infra-red definitely requires that m be given the values $1/2, 3/2, 5/2, \cdots\cdots \infty$.

Kratzer[10] has advanced arguments supporting the contention that half quantum numbers are only apparent, and that in the quantization of the entire dynamical system the quantum numbers assume integral values. In the hydrogen halides he supposes to be present due to the motion of electrons an angular momentum vector perpendicular to the line joining the nuclei and of magnitude $\frac{1}{2}h/2\pi$. In order for the total angular momentum to be an integral multiple of $h/2\pi$ the rotation of the molecule would have to contribute the amount $mh/2\pi$, with m having half-integral values. Kramers and Pauli[11] suggest that the electronic angular momentum vector has the magnitude $h/2\pi$ and makes an angle of 30° with the line joining the nuclei, so that its component normal to this line is $\frac{1}{2}h/2\pi$. It is evident that these theories would lead to expressions for $\overline{\overline{\cos\theta}}$ differing from that used in this paper. It has not seemed worth while to evaluate these expressions; expecially in view of the fact that hydrogen chloride is diamagnetic, for if the presence of electronic angular momentum requires the presence of a magnetic dipole the theories of Kratzer and Kramers and Pauli would require it to be paramagnetic.

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[10] Kratzer, Ann. d. Physik, **71**, 72 (1923).

If it be assumed, then, that in some cases quantum numbers can have half-integral values, there are two possibilities for n, for it can be placed equal to $0, \pm 1, \pm 2, \cdots \pm(m-\frac{1}{2})$, or to $\pm 1/2, \pm 3/2, \pm 5/2, \cdots \pm m$. It is necessary to include $n=0$ in the first group, for with $m=\frac{1}{2}$ this is the only integral value allowed. It can be shown unambiguously that the values $n=0, \pm 1, \pm 2, \cdots \pm(m-\frac{1}{2})$ cannot be correct. For with them the equation

$$C=\frac{1}{2\sigma}\,\frac{\sum\limits_{r=1}^{\infty}\left(-\frac{1}{4(r-\frac{1}{2})^3}\right)e^{-\sigma(r-\frac{1}{2})^2}}{\sum\limits_{r=1}^{\infty}(2r-1)e^{-\sigma(r-\frac{1}{2})2}} \tag{23}$$

is obtained in place of Eq. (13); this equation, however, leads to negative values of C for all values of σ. Consequently Eq. (23) requires that at all temperatures the hydrogen chloride gas possess a *negative* polarization due to permanent dipoles. *The experimental measurements of the dielectric constants of the hydrogen halides accordingly rule out the quantum-number assignment*
$m=1/2, 3/2, 5/2, \cdots \infty, n=0, \pm 1, \pm 2, \cdots, \pm(m-\frac{1}{2})$.

The remaining assignment, with $n=\pm 1/2, \pm 3/2, \pm 5/2, \cdots, \pm m$, has then been used in this paper. It is to be emphasized that this assignment is not compatible with the idea that true quantum numbers are integral, and that half-quantum numbers result from the presence of an angular momentum vector due to the motion of electrons.

The possibility of weak quantization. The sharpness of the band spectra shows that the quantization with respect to the total quantum number m is strong; this is to be expected, for the molecule goes through many rotations between collisions. On the other hand weak spatial quantization might occur.

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[11] Kramers and Pauli, Zeits. f. Physik, 13, 351 (1923).

If all orientations were equally probable; i. e., if there were completely weak spatial quantization, the average value of $\cos\theta$ for rotators with quantum number m would be given by Eq. (9) with n^2/m^2 replaced by the average value of $\cos^2\beta$, which is $\frac{1}{3}$; β is the angle between the axis of rotation of the molecule and the lines of force of the applied field. $\overline{\overline{\cos}}\theta$ would then be zero; in other words, there would be no polarization due to permanent dipoles. This is in agreement with the result of Alexander,[12] who showed that *on the classical theory of all of the polarization is caused by molecules whose total energy is less than μF.* Since there are actually no such molecules present, polarization must arise from some other mechanism. This mechanism is spatial quantization.

We have assumed strong spatial quantization in determining the values of μ; if this assumption is incorrect, the values given are too low. But if the spatial quantization had been weak the dielectric constant would have varied with the field strengths applied. Such a variation has never been reported; Zahn and Bädeker, using different experimental methods and undoubtedly different field strengths, obtained the same values for ϵ for hydrogen chloride. It accordingly seems highly probable that there is strong spatial quantization with respect to the applied electric field.

A brief account of this work has been published in the Proceedings of the National Academy of Sciences.[13]

GATES CHEMICAL LABORATORY,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
PASADENA, CALIFORNIA.
February, 1926.

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[12] Alexandrow, Phys. Zeits. **22**, 258 (1921).

[13] Pauling, Proc. Nat. Acad., **12**, 32 (1926).

THERMIONIC PHENOMENA CAUSED BY VAPORS OF RUBIDIUM AND POTASSIUM

By Thomas J. Killian*

Abstract

Thermionic effects similar to those studied by Langmuir and Kingdon for caesium have been found for rubidium and potassium. Because of the difference in the electron affinity of tungsten (4.53 volts) and that of an atom of rubidium or potassium (4.16 and 4.32 volts respectively) positive ions are formed which at filament temperatures above 1000° are drawn to the cylindrical collector from the coaxial filament. Below this temperature the ions are adsorbed on the surface of the filament and decrease its work function raising the electron emission. The degree of *thermal ionization* at various filament temperatures is found to be within the experimental error of that determined from Saha's equation. At low temperatures the filament is partially covered by adsorbed ions and the *electron emission* increases exponentially with the reciprocal of the temperature. A transition region is reached as the average life of an atom on the surface becomes shorter and then the emission decreases logarithmically with the reciprocal of the temperature. The curves and values are given. The *positive ion emission* increases logarithmically with the reciprocal of the temperature until a certain fraction of the atoms striking the filament is ionized. Further increase in temperature causes every atom to be ionized. The coincidence of experimentally determined points with the theoretical space charge curve shows each ion to have the mass of a single atom in the range of pressures studied.

Vapor pressure of rubidium and potassium.—The vapor pressure of rubidium and potassium is calculated from the maximum ion current; for rubidium $\log p = 10.55 - 4132/T$ and for potassium $\log p = 11.83 - 4964/T$; here p is in bars.

THE thermionic effects caused by caesium vapor have previously been studied by Langmuir and Kingdon.[1,2,3] This work was undertaken in order to compare the similar effects caused by the vapors of the other alkali metals.

A tungsten filament heated above 1200°K in caesium vapor was found to convert every caesium atom striking it to a caesium ion. This is due to the fact that the electron affinity of tungsten (work function) is 4.53 volts while that of caesium (ionizing potential) is only 3.88 volts. It was shown that by decreasing the work function of the filament to 2.69 volts by allowing a monatomic layer of thorium atoms to accumulate on the surface,[4] the positive ion emission became negligible.[3] The positive ions formed at the pure tungsten surface must be drawn to it by an image force. Below 1200°K they evaporate so slowly that the surface becomes partially covered by adsorbed caesium ions. This however lowers the electron affinity of the surface and when about 20 percent is covered the electron affinity of the surface is less than that of the atoms of caesium and no more ions are formed. However this decrease in the electron affinity greatly increases the electron emission from the surface. At a pressure of caesium corresponding to 20°C they obtained 4×10^{-5} amps. per cm^2 at a filament temperature of 670°K. Since the ionizing potentials of rubidium and potassium are 4.16 volts and 4.32 volts respectively it was expected that vapors of these metals would produce similar effects.

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[1] I. Langmuir and K. H. Kingdon, Science **57**, 58 (1923).

[2] K. H. Kingdon and I. Langmuir, Phys. Rev. **21**, 380 (1923).

[3] I. Langmuir and K. H. Kingdon, Proc. Roy. Soc. A **107**, 61 (1925).

APPARATUS

The tubes contained a pure tungsten filament of diameter 0.0051 cms mounted coaxially with a nickel cylinder of diameter 1.905 cms. In some tubes this collector was 2.54 cms long and in others 5.08 cms. This cylinder was between two other cylinders of the same diameter and of length 7.62 cms, the distance between them being from .08 cms to .16 cms. At each end of the filament a 6 mil tungsten spring took up the expansion due to heating. The tubes were exhausted by means of a condensation pump while being baked out at 360°C for 3 hours. The collectors were freed from gas by being heated to redness by means of induced high frequency currents. The filaments were flashed at a high temperature while the tubes were on the pump.

The smaller plate currents were measured by means of a Leeds and Northrup testing galvanometer and the larger ones by means of a microammeter. A General Electric deflection potentiometer gave the filament current. With the tube as constructed the two outer cylinders act as guard cylinders and the temperature of the part of the filament in the center cylinder is not affected more than 0.1 percent at 750°K by cooling effect of the leads. The temperature scale used is that of Forsythe and Worthing.[5]

THERMAL IONIZATION

In the paper[3] referred to, the modified form of Saha's equation was used to determine the degree of thermal ionization. The equilibrium constant is given by

$$K_n = n_e n_p / n_a$$

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[4] I. Langmuir, Phys. Rev. **22**, 357 (1923).

[5] W. E. Forsythe and A. G. Worthing, Astrophys. J. **61**, 146 (1925).

where n_e, n_p and n_a are respectively the number of electrons, of positive ions and of atoms per unit volume. For any alkali metal

$$\log_{10} K_n = 15.365 + \frac{3}{2}\log_{10} T - \frac{11,600\ V}{2.303\ T}$$

where V is the ionizing potential and T the absolute temperature. This expression for K_n has the dimensions of number per unit volume. Experimentally we have to do with currents and may define

$$K_I = I_e I_p / I_a$$

Where I_e and I_p are respectively the electron and positive ion emission per unit area at any filament temperature and I_a is the current density corresponding to the ionization of every atom hitting the filament. Then

$$K_I = eK_n\sqrt{\frac{kT}{2\pi m_e}} = 2.481\times 10^{-14}\ K_n\ \sqrt{T}\quad \text{amp. per cm}^2$$

For rubidium

$$\log_{10} K_I = 1.7792 + 2\log_{10} T - 20{,}932/T$$

The equilibrium constants found experimentally at various filament temperatures were about one-half those calculated theoretically. That is with a filament temperature of 1302°K the equilibrium constant was found to correspond to a filament temperature of 1273°K. The logarithm of the emission was plotted against the square root of the voltage to correct for the Schottky[6] effect. At any filament temperature the slopes were found to be the same for both ions and electrons and about double that calculated from Schottky's formula. Thus it is seen that the results obtained for the equilibrium constant are probably within the experimental error furnishing further verification of Saha's assumptions.

ELECTRON EMISSION

As in the case of caesium at low temperatures a tungsten filament in rubidium or potassium vapor becomes covered with a layer of adsorbed atoms. As the temperature of the filament is increased the electron emission increases logarithmically with the reciprocal of the temperature. However as the filament temperature is further increased the current reaches a maximum and then decreases as the temperature is raised due to the evaporation of the atoms at the higher temperatures.

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[6] W. Schottky, Phys. Zeits. **15**, 872 (1914).

By flashing the filament in oxygen before introducing the alkali metal the filament becomes covered with a layer of oxygen atoms which is not evaporated off below 1600°K. This layer tends to hold the alkali metal on at higher temperatures and thus the emission at a given filament temperature is higher from an oxygen coated filament in the alkali metal vapor than from a pure tungsten filament.

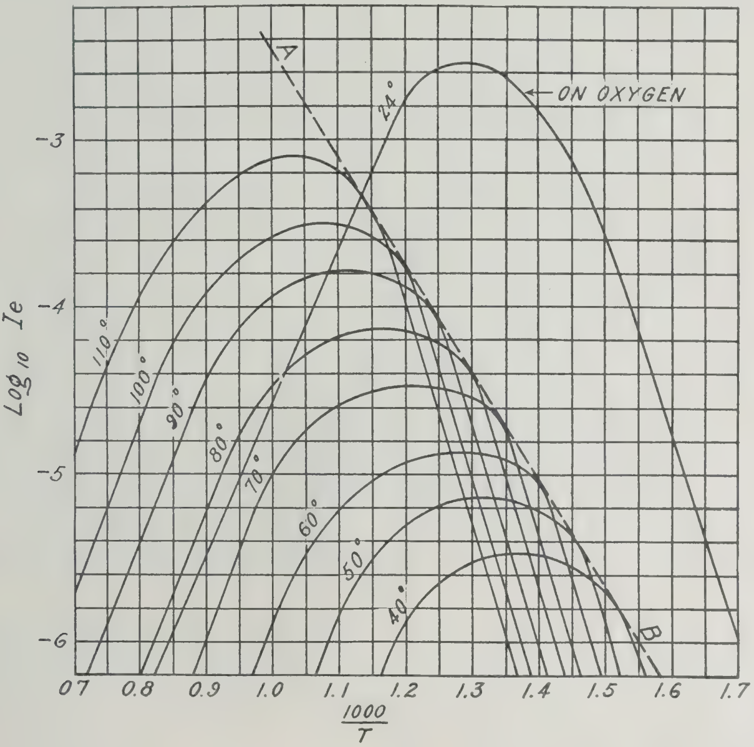

Fig. 1. Electron emission in amperes per cm² from a tungsten filament in rubidium vapor at various pressures. Temperature of bulb in °C on each curve.

Figs. 1 and 2 give the family of curves of the electron emission of filaments in the presence of rubidium and of potassium vapor. The ordinates are the common logarithms of I_e, the electron current in amp per cm^2, and the abscissas are the reciprocals of the absolute temperature of the filament multiplied by 1000. The temperature of the bulb which fixed the vapor pressure is given in degrees Centigrade on each curve. Before each reading the filament was flashed at a high temperature to drive off any impurities.

In the curves with the metal adsorbed on the pure tungsten surface we see that, as in the case of caesium, each curve consists of three parts: (1) a low-temperature region where the logarithm of the emission is a straight line when plotted against the reciprocal of the temperature; (2) an intermediate region where the plot in Figs. 1 and 2 is curved; (3) a high temperature region where again the logarithm of the current is a linear function of the reciprocal of the temperature. The curves are very much alike and differ principally in being displaced parallel to their envelope *A B*. These displacements are proportional to the logarithms of the pressures of the vapor. Thus in regions (1) and (2) we may say that approximately

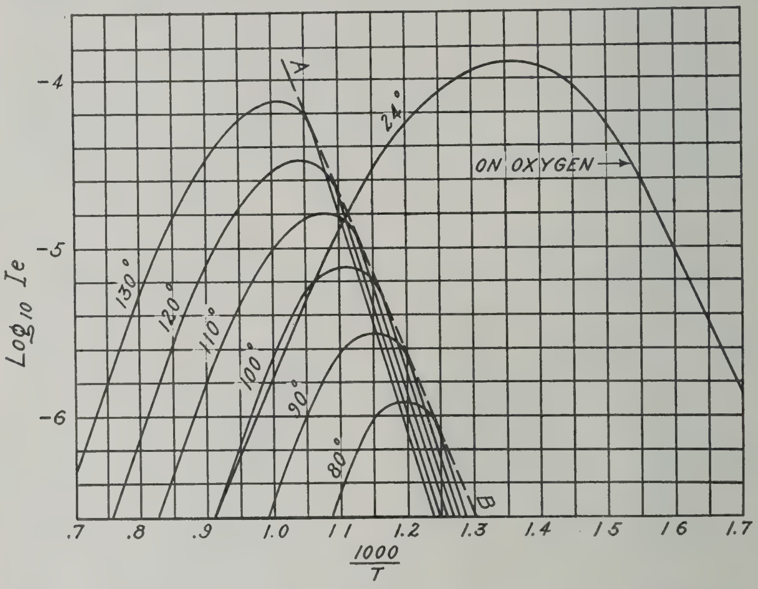

Fig. 2. Electron emission in amperes per cm² from a tungsten filament in potassium vapor at various pressures. Temperature of bulb in °C on each curve.

$$I_e=\alpha p^{\gamma}\epsilon^{-\beta/T}$$

From the curves in Figs. 1 and 2 we obtain the results shown in Table I for the constants α, β and γ.

I is in amp. per cm² and *p* in bars.

Positive Ion Emission

The positive ion emission at any vapor pressure increases exponentially with the reciprocal of the filament temperature until the emission is about 20 percent of the maximum when there is a definite discontinuity. Further increase in temperature causes every atom to be ionized. Thus, as in the case of caesium, there is the same evidence of the existence of two surface phases on the filament, one in which only a fraction of the atoms is ionized and the other in which all of them are. There is a definite boundary between them and the rate at which

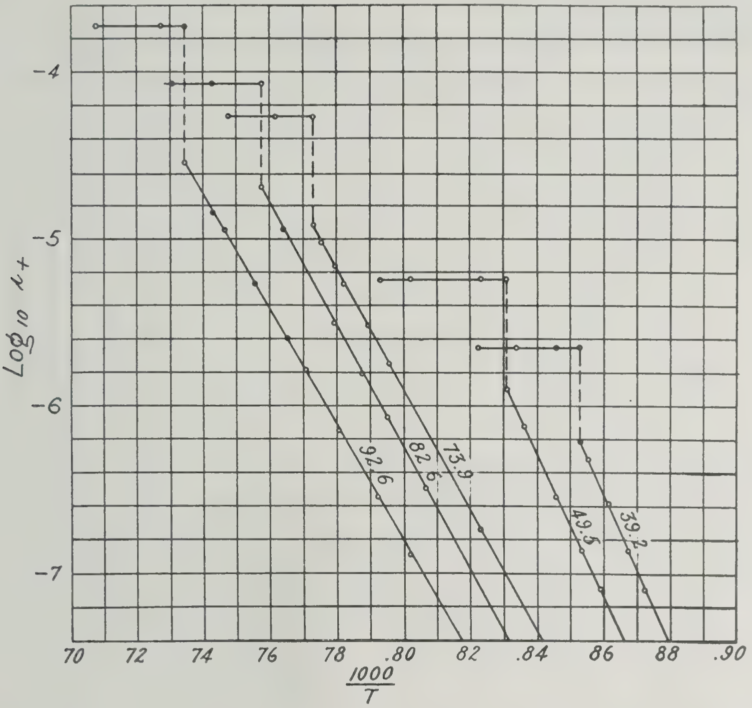

Fig. 3. Positive ion emission in amperes from a tungsten filament of area 0.0405 cm² in rubidium vapor at various pressures. Collector voltage = −200. Temperature of bulb in °C on each curve.

TABLE I

Values of the constants α, β, γ of Eq. (1).

Filament coating	α	β	γ
Rubidium on tungsten			
Region (1)	2.86×10^{12}	32,000	−1.12
Region (3)	2.08×10^{-12}	−24,000	+2.52
Rubidium on adsorbed oxygen			
Region (1)		28,000	
Region (3)		−23,000	
Potassium on tungsten			
Region (1)	5.9×10^{9}	30,800	−0.328
Region (3)	1.27×10^{-13}	−25,600	+2.66
Potassium on adsorbed oxygen			
Region (1)		19,700	
Region (3)		−23,000	

it moves along the filament can be easily measured by observing the microammeters in series with the three collectors. This velocity is found to depend upon the collector voltage and filament temperature. Langmuir and Kingdon[7] have obtained for caesium curves similar to those in Figs. 3 and 4.

If every atom is converted into a single ion a measure of the maximum positive ion current would be an accurate way of determining the vapor pressure. The currents limited by space charge with long coaxial cylinders is given by[8]

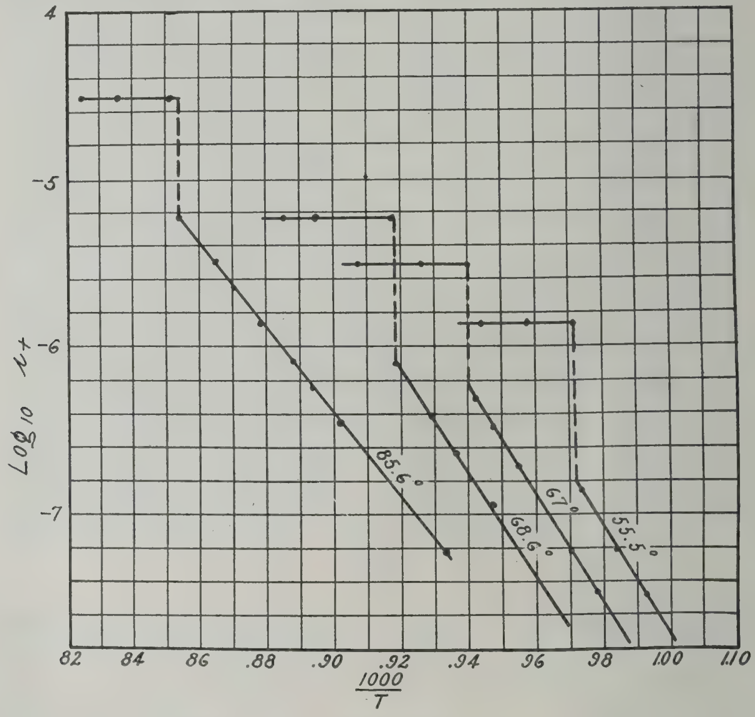

Fig. 4. Positive ion emission in amperes from a tungsten filament of area 0.081 cm² in potassium vapor at various pressures. Collector voltage = −200. Temperature of bulb in °C each on curve.

$$i=14.68\times 10^{-6}\sqrt{m_e/m_p}\;V^{3/2}/r\beta^2$$

here i is in amperes per cm length of filament, m_e and m_p the masses of an electron and positive ion respectively, V the potential of the collector below the filament in volts, r the radius of the collector and β^2 a function of the ratio of the diameters of the collector and filament. In this case $\beta^2 = 1.04$.

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[7] Langmuir and Kingdon, unpublished work.

[8] Langmuir, Phys. Rev. **2**, 450 (1913).

In Figs. 5 and 6 are plotted the theoretical ion currents limited by space charge assuming the mass of a positive ion to be that of a single atom. The points were experimentally determined and corrected for contact potential. They check very accurately with the theoretical curve, showing that in the range of pressures studied the mass of the positive carrier is that of a single atom.[9]

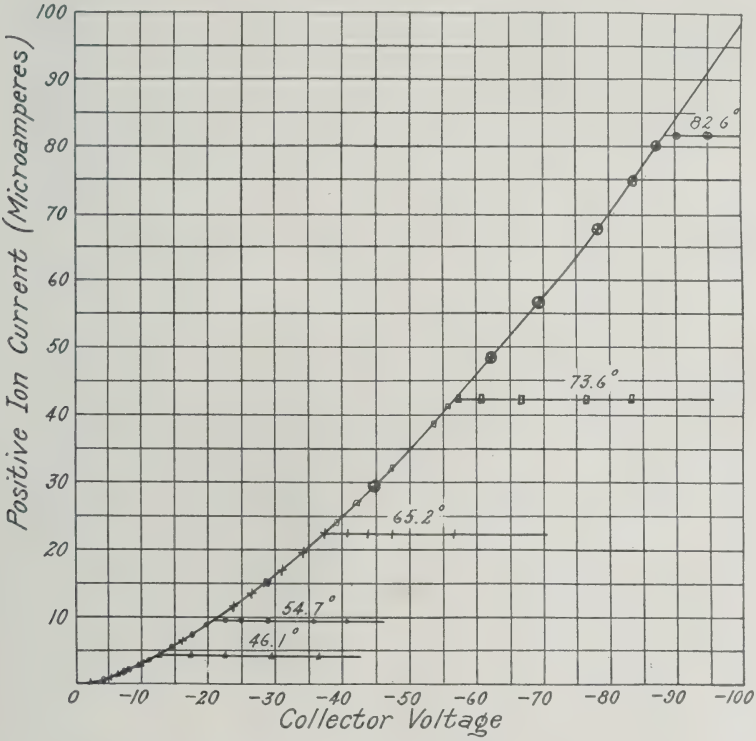

Fig. 5. Rubidium positive ion current limited by space charge at various vapor pressures. Full line is theoretical curve $I_+ = 0.0985\ V^{3/2}$. Temperature of bulb in °C on each curve.

Vapor Pressure

From the kinetic theory we know that the maximum positive ion current i_+ is $ep/\sqrt{2\pi mkT}$ abamperes per cm^2 where e is the charge on an electron, p the pressure in bars, m the mass of an atom, k the Boltzmann constant and T the absolute temperature.

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[9] Since this work was done H. E. Ives in Jour. Frank. Inst. **201,** 62 (1926) claims this is not true at vapor pressures below those corresponding to a temperature of 60°C for caesium, rubidium and potassium.

For rubidium

$$i_+ = .457\ p/\sqrt{T} \text{ amperes per cm}^2$$

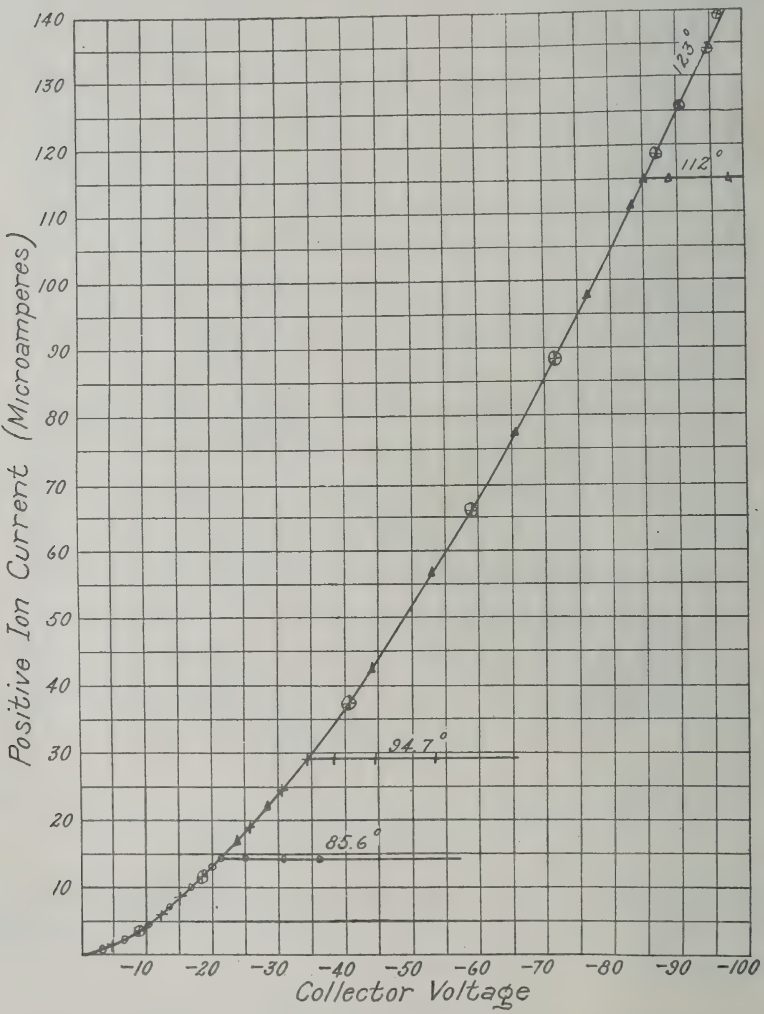

Fig. 6. Potassium positive ion current limited by space charge at various vapor pressures. Full line is theoretical curve $I_+ = 0.1452\ V^{3/2}$. Temperature of bulb in °C on each curve.

and for potassium

$$i_+ = .657\ p/\sqrt{T} \text{ amperes per cm}^2$$

Fig. 7 presents the vapor pressures of caesium, rubidium and potassium found by this method. The curve for caesium is taken from the results of Langmuir and Kingdon.[3]

For rubidium

$$\log_{10} p = 10.55 - 4132/T$$

For potassium

$$\log_{10} p = 11.83 - 4964/T$$

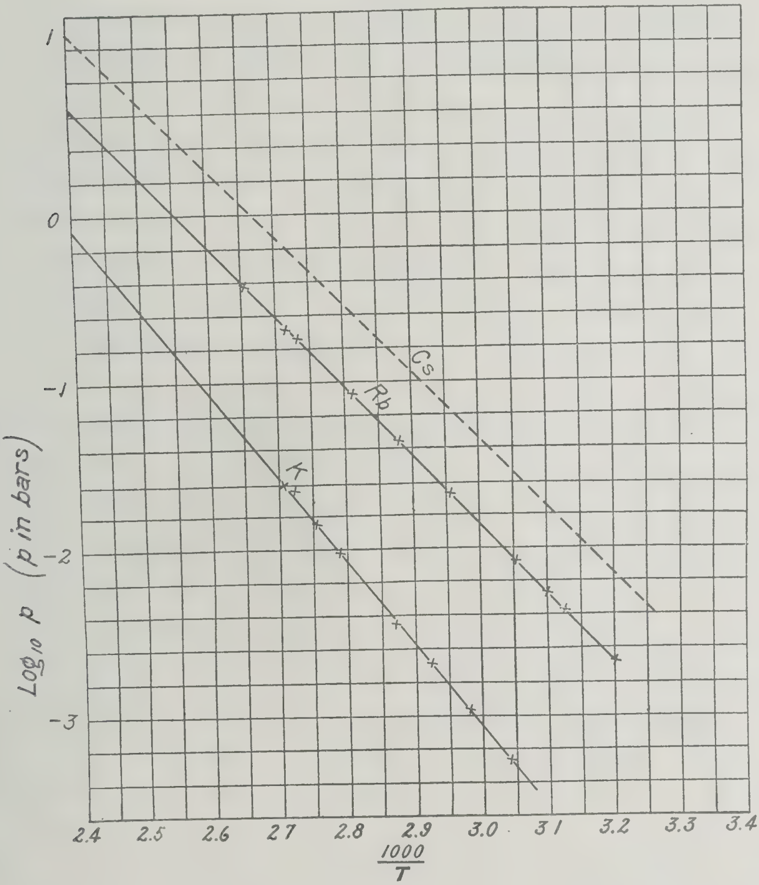

Fig. 7. Vapor pressures of Cs, Rb, and K at various temperatures as determined by the positive ion method.

I desire to express my gratitude to Dr. Irving Langmuir and Dr. K. H. Kingdon for suggesting this work and aiding me in its completion.

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General Electric Company,
Schenectady, New York,
February 9, 1926.

MAY, 1926 PHYSICAL REVIEW VOLUME 27

THE MOTION OF ELECTRONS IN HYDROGEN AND HELIUM

By H. B. Wahlin

Abstract

Mobilities of electrons in H_2 and He at 760 mm pressure have been measured by the Rutherford alternating potential method for fields ranging from 0.5 to 46 volts/cm. The limiting mobilities for zero field are calculated to be, for H_2, 6,700 cm/sec per volt/cm and for He, 10,840 cm/sec per volt/cm.

Energy loss of an electron on impact in H_2 and He.—*K. T. Compton's theory of electronic mobilities* is shown to fit the observed variation of mobility with field strength provided it be assumed that the fraction of its energy an electron loses on impact is, in H_2, 2.16, and in He, 8.6 times what it would be were the collisions elastic.

Mean free path of electrons in H_2 and He.—From the limiting values of the mobilities at zero field it is calculated that the mean free path of electrons in thermal equilibrium with the gas is for H_2 at 1 mm pressure, 0.0408 cm, and for He at 1 mm pressure, 0.066 cm. These values are approximately half the kinetic theory values.

THE motion of electrons through a gas under the action of an electric field has been studied by Townsend and Bailey,[1] Loeb,[2] and the writer.[3] Using a method in which the velocity in the direction of the field was determined by a magnetic deflection and in which the velocity of agitation was determined from the lateral diffusion of the electron beam, Townsend and Bailey have succeeded in showing that the velocity of drift of the electrons per unit field intensity is not independent of the field as is the case with ions, but decreases with increasing voltage. This is due to two causes. First, the electrons are not in thermal equilibrium with the gas, but, because of energy gained in the field, reach a thermal velocity which exceeds that of the gas. Secondly, as has been shown by Ramsauer[4] the electron free path is not a constant, but decreases with increasing velocity of agitation for low velocities and increases again for higher velocities.

Townsend's method is not very well adapted to a study of the motion of electrons in low fields, and for that reason it was thought best to extend the measurements on the determination of electron free paths to such small fields that the electrons may be considered to be in thermal equilibrium with the molecules. A second purpose of the present investigation was to see if a comparison could be made between the experimental results and a theoretical equation for electron mobilities derived by K. T. Compton.

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[1] J. S. Townsend, J. Franklin Inst. 563 (Nov. 1925).

[2] L. B. Loeb, Phys. Rev. **20,** 397 (Nov. 1922); **23,** 157 (Feb. 1924).

[3] H. B. Wahlin, Phys. Rev. **23,** 169 (Feb. 1924).

[4] C. Ramsauer, Ann. d. Physik **64,** 513 (1921); **66,** 546 (1922).

The method used was the Rutherford alternating potential one with a Hartley oscillating circuit as a source of alternating potential. It differed only in detail from the one described in an earlier paper dealing with electron motion in nitrogen. The alternating potential was measured by a Kelvin multicellular voltmeter from 120 to 30 volts and by an electrometer with a phosphor bronze suspension below 30 volts.

The hydrogen was purified by passing it over hot copper, through a tube containing fused calcium chloride, through a second tube containing potassium hydroxide and slowly through a system of tubes 225 cm long containing phosphorus pentoxide.

In order to purify the helium (which originally contained about 2 percent oxygen and nitrogen) three traps each containing about 170 cc of finely divided charcoal were used. The charcoal had been activated with steam and was baked at a temperature of 300°C for 24 hours or more. The third trap was so arranged that it was connected permanently to the chamber holding the gas, and the helium circulated through this continuously by convection, while the readings were being taken. No change in the results could be noticed after circulating for a period of 24 hours so that it seems reasonable to assume that the gas was pure.

All determinations were made at a pressure of 760 mm. In obtaining the mobility curves, the frequency was kept constant and the alternating potential varied. From the intercepts of the mobility curves obtained by plotting the current against field intensity, approximate values of the mobility were computed from the equation

$$u=\pi nd/\sqrt{2x} \tag{1}$$

where n is the frequency, d the distance between the plates, and x the effective value of the alternating field.

Figs. 1 and 2 illustrate the types of curves obtained in H_2 and He respectively. It is to be noted that the intercepts are well defined so that any error arising from an ill-defined intercept was slight. In the case of curves obtained with low frequencies, i. e. where the intercept came in low fields, a number of curves were obtained without changing the frequency, and the mobility computed from the average value of the intercept thus obtained.

The mobilities computed from Eq. (1) are plotted as a function of the field intensity in Figs. 3 and 4, Fig. 3 for H_2 and Fig. 4 for He. As the mobility is not a constant, the values for higher fields must be considered as approximate only, since in the derivation of Eq. (1) it is assumed that the mobility is independent of the field, and in general this is far from being the case. However, an examination of these curves will show that for low fields the mobility is so nearly independent of the field that Eq. (1) is applicable and the true value of

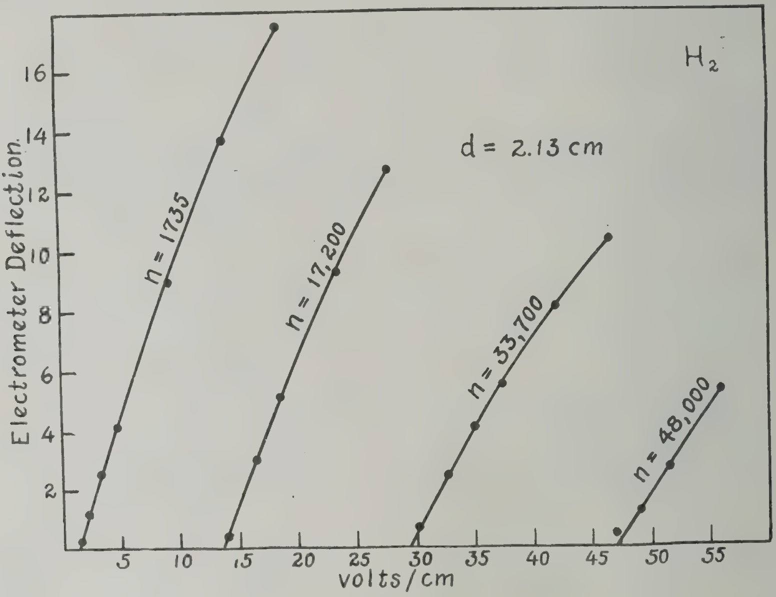

Fig. 1.

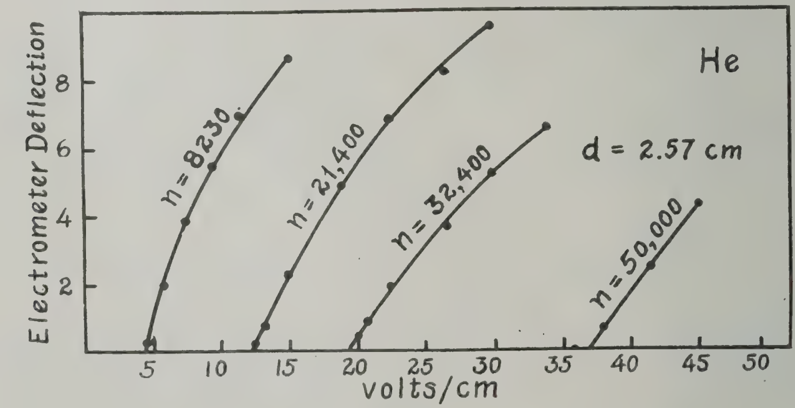

Fig. 2.

the limiting mobility may be obtained directly from it. The values thus obtained are:

$$u_{H_2} = 6700 \text{ cm/sec per volt/cm},$$
$$u_{He} = 10{,}840 \text{ cm/sec per volt/cm}.$$

The use of the alternating potential method for determining mobilities has been criticized because the electrons do not move through the gas with the thermal velocity corresponding to the instantaneous values of the field. Compton has shown, however, that the distance the electrons must travel to gain even 99 percent of their terminal energy is small at a pressure of 760 mm, so that the error would be slight. There would be a phase lag between the terminal energy and the instantaneous value of the field driving the electrons from one plate to the other. In other words, during that part of the half-cycle when the voltage is rising, the thermal energy is less than it should be, and during the part of the half-cycle when the voltage is decreasing it is greater. These two errors would tend to counterbalance each other.

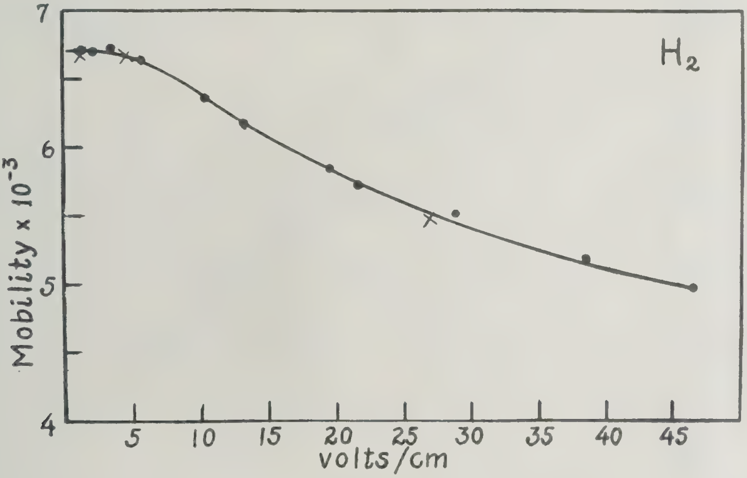

Fig. 3. Variation with field strength of electron mobilities in hydrogen.

In order to settle definitely any doubt concerning the question of terminal energy, the distance between the plates was varied from 2.13 cm to 4.0 cm in the case of H_2. The values represented by the dots (Fig. 3) were obtained with the former distance, and the values corresponding to the crosses with the latter. It will be noticed that they do not differ appreciably, so that any effect due to a non-terminal state is slight.

TEST OF COMPTON'S EQUATION FOR MOBILITY

As stated above, Eq. (1) is applicable only over that range of field intensities for which the mobility may be considered as constant. When the field becomes so large that the thermal energy of the electrons differs appreciably from the molecular, the mobility will decrease because of the decreased time between impacts. In general, then, the mobility will be a function of the field. K. T. Compton[5] has derived this function and has shown that

$$u=\frac{.815\,e\lambda}{\sqrt{m}\left[\alpha T+\left(\alpha^2T^2+1.76\lambda^2e^2x^2/f\right)^{\frac{1}{2}}\right]^{\frac{1}{2}}}$$

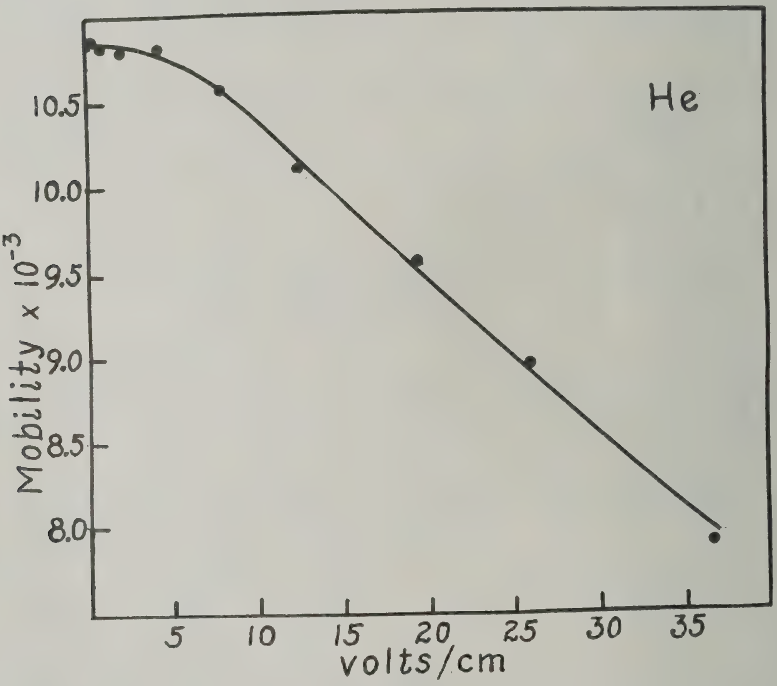

Fig. 4. Variation with field strength of electron mobilities in helium.

where e is the electronic charge, λ the mean free path, αT the thermal energy of the molecules, and f the fraction of its energy an electron loses on impact with a molecule.

This equation may be written in the form

$$u=\frac{a}{\left[1+(1+Bx^2)^{\frac{1}{2}}\right]^{\frac{1}{2}}}$$

if it is assumed that λ is independent of x.

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[5] K. T. Compton, Phys. Rev. **22**, 333 (1923).

The equation of motion of the electrons would then be

$$\frac{dy}{dt}=\frac{ax}{[1+(1+Bx^2)^{\frac{1}{2}}]^{\frac{1}{2}}}$$

where x is the instantaneous value of the field, and dy/dt is the velocity in the direction of the field.

In the case under discussion since a sine field was employed, we get

$$\frac{dy}{dt}=\frac{aX\sin 2\pi nt}{[1+(1+BX^2\sin^2 2\pi nt)^{\frac{1}{2}}]^{\frac{1}{2}}} \tag{2}$$

Thus a direct check of Compton's equation is impossible in this case. However, it is possible to compare the experimentally determined frequency necessary to obtain an intercept with a given field with those obtained by a solution of this differential equation. Eq. (2) becomes for this case

$$\int_0^d dy=\int_0^{1/2n}\frac{aX\sin 2\pi nt\,dt}{[1+(1+BX^2\sin {}^2 2\pi nt)^{\frac{1}{2}}]^{\frac{1}{2}}}$$

Placing $2\pi nt=\theta$ and solving for n we get

$$n=\frac{aX}{\pi d}\int_0^{\pi/2}\frac{\sin\theta\,d\theta}{[1+(1+BX^2\sin^2\theta)^{\frac{1}{2}}]^{\frac{1}{2}}}$$

This is an elliptic integral and on reduction gives

$$n=\frac{a\sqrt{2r}}{\pi d\sqrt{B}}[2E(k,\varphi)-F(k,\varphi)] \tag{3}$$

in which

$$r=\sqrt{BX^2+1}\,,\qquad k=\sqrt{\frac{r+1}{2r}}\text{ and }\varphi=\sin^{-1}\sqrt{\frac{r-1}{r+1}}$$

The values of a may be determined immediately from the limiting mobility as the field approaches zero, since in this case Compton's equation reduces to the form $u=a/\sqrt{2}$. We thus get

$a_{\mathrm{H}} = 9{,}490$ cm/sec per volt/cm
$a_{\mathrm{He}} = 15{,}350$ cm/sec per volt/cm.

The values of B which fit the experimental results most closely are

$B_{\mathrm{H}_2} = .003$
$B_{\mathrm{He}} = .004$

Tables I and II give the frequencies computed from Eq. (3), together with those experimentally determined.

TABLE I

Hydrogen

$a=9490$,	$B=.003$,	$d=2.13$ cm
Effective value of field	n (calc.)	n (obs.)
1.23	1730	1735
2.09	2960	2959
3.52	4955	5000
5.73	8000	7990
10.40	14,000	14,000
13.2	17,400	17,200
19.5	24,300	24,000
21.7	26,600	26,200
28.9	33,300	33,700
38.5	41,200	42,200
46.0	46,700	48,000

TABLE II

Helium

$a=15,350$,	$B=.004$,	$d=2.57$ cm
Effective value of field	n (calc.)	n (obs.)
.554	1055	1061
1.107	2120	2090
2.18	4160	4110
4.33	8220	8230
7.94	14,770	14,720
12.40	22,100	21,400
19.28	32,200	32,400
26.00	40,600	40,750
36.65	52,300	50,000

The agreement between the experimental and calculated values is quite close. For the higher frequency there is a slight variation which may be due to experimental errors.

CALCULATION OF MEAN FREE PATH

Since Compton's equation satisfied the experimental data so closely it must be concluded that over the range of voltages used in these experiments the mean free path is a constant and independent of the electron velocity. This is not the case in nitrogen, as shown in the article referred to above. The values for the mean free path may most readily be computed from the limiting mobility, using Townsend's equation, viz.

$$u=.75e\lambda/m\bar{v}$$

The values thus calculated for a pressure of 1 mm placing $\bar{v}=1.065\times10^7$ cm/sec. at 20°C, together with the kinetic theory values ($4\sqrt{2}$ times the molecular free path) are

	Experimental λ	Kinetic theory λ
H_2	.04080 cm	.0842 cm
He	.0660	.1313

The experimental values are thus seen to be lower than the kinetic theory values. This, however, is not in general the case. Since the experimental value of λ found for N_2 is .0996 cm at 1 mm pressure whereas according to kinetic theory reasoning it should be lower than both λ_{H_2} and λ_{He}.

ENERGY LOSS OF AN ELECTRON ON IMPACT

In the discussion of Compton's equation above, we used it in the general form, simply assuming that the energy loss on impact is a fraction f of the electronic energy. From the experimentally determined value of B it is possible to calculate this fraction f. Since

$$B=1.76\lambda^2e^2/f\alpha^2T^2$$

we get, remembering that x is measured in volts,

$$f_{H_2}=1.17\times10^{-3}$$
$$f_{He}=2.32\times10^{-3}$$

If the impacts are elastic Compton has shown that

$$f=2m/M$$

where m is the electronic and M the molecular mass. From this we get

$$f_{H_2}=.541\times10^{-3}$$
$$f_{He}=.270\times10^{-3}$$

The observed fraction is about 2.16 times what it should be on the basis of elastic impacts in H_2 and 8.6 times too large for He. The fraction lost is very small in either case and is independent of the energy of the electron at impact over the range of energies covered in these experiments. The fact that f for He is greater than that for H_2 may be due to the presence of some impurity not readily absorbed by the charcoal although it is difficult to imagine what it could be. No electronegative impurities were present, as shown by the high value obtained for the limiting mobility, and it seems reasonable therefore to conclude that other impurities were present in very small quantities.

Fortunately the mobility is independent of x and therefore also of f in low fields, so that the effect on the limiting mobility would be negligible, unless the molecular dimensions of the impurity differ enormously from those of helium.

UNIVERSITY OF WISCONSIN,
MADISON, WISCONSIN,
January 25, 1926.

VISIBILITY PHENOMENA WITH INTERFERENCE BY MULTIPLE REFLECTIONS

By Lachlan Gilchrist

Abstract

Visibility of interference fringes due to multiple reflections of approximately monochromatic light.—Approximate expressions are developed for the intensity and visibility of interference fringes for both transmitted and reflected light when any number of multiple reflections exist and the source of light is one of small width. Where the number of reflections is large, the visibility is $V=2b^2C/P$ and $V=(1-b^2)C/P$ respectively, C and P depending on the distribution of intensity in the source and having the significance which was given them by Michelson and Rayleigh b is the coefficient of reflection at the first reflecting surface. The effects of the coefficients of reflection and absorption are examined and it is indicated that the method of visibility with interferometers which depend on multiple reflection may be used to advantage in the study of the fine structure of such spectra as those of hydrogen and helium, not only in order to obtain the components but also to determine the character of each component. It is also indicated that the development may be extended to x-ray spectra in which series of multiple reflections from numerous planes exist.

THE growing necessity of obtaining high resolution of the components of a source of radiation makes it desirable that the method of visibility of interference fringes developed by A. A. Michelson should be investigated for the case where the interference is obtained under the conditions of multiple reflections. Resolution of a very high order may be obtained and components very close in wave-length are revealed by this method, but it has the further distinct advantage that it gives the distribution of intensity in the radiation of various wave-lengths emitted by components of the source. Moreover recent developments in the quantum theory make it desirable to obtain this information of the fine structure, particularly of hydrogen and helium spectra.

Interference of homogeneous radiation of wave-number m as ordinarily obtained is represented by

$$I=2A^2(1+\cos 4\pi Dm). \tag{1}$$

For a source of small "width" this becomes

$$I=2\int_{-x}^{x} F(x)\{1+\cos 4\pi D(\overline{m}+x)\}\,dx. \tag{2}$$

If visibility is defined by the expression

$$V=\frac{I_{max}-I_{min}}{I_{max}+I_{min}} \tag{3}$$

and if the distribution of intensity in the source follows the probability law,

$$V=C/P=\frac{\int_{-\infty}^{+\infty}\exp\left[-h^2x^2\right]\cos 4\pi Dx\,dx}{\int_{-\infty}^{+\infty}\exp\left[-h^2x^2\right]dx}=\exp\left[-(2D)^2\pi^2/h^2\right] \tag{4}$$

Where there are several components in the source the visibility is expressed by

$$U^2=\frac{\sum r^2+2\sum rr'\cos 4\pi D(d'-d)}{(\sum r)^2}V^2 \tag{5}$$

If the width of the source be considered as due to a Doppler effect in which Maxwell's law of distribution of velocities exists it was shown by the late Lord Rayleigh that

$$V=\exp\left[-\pi(\pi\Delta v/\lambda c)^2\right] \tag{6}$$

and (4) has been expressed in terms of a defined width $\bar{a}$ by Michelson thus

$$V=\exp\left[-(2D)^2\pi^2\bar{a}^2/4\log 2\right] \tag{7}$$

From (6), Δ corresponding to a definite value of V was obtained and used in (7) for the same value of V, viz. one-half the maximum V. This gave for the width

$$W=(v\lambda/c)\left(2\sqrt{\pi\log 2}\right) \tag{8}$$

or where the freedom of the source is modified by density

$$W=(v\lambda/c)\left(2\sqrt{\pi\log 2}+\lambda/\rho\right) \tag{9}$$

where ρ is the mean free path of the source which was assumed to be atomic in character.

If the source is atomic in character and depends on the atomic weight and the temperature, then (9) may be expressed

$$W=\frac{\lambda}{\sqrt{m}}\,\frac{v_0}{c}\sqrt{\frac{T}{T_0}}\left(2\sqrt{\pi\log 2}+\lambda/\rho\right) \tag{10}$$

In the application of these formulas Michelson made use of a comparator to compare the visibility for any path difference with the maximum visibility which he defined as unity.

Now the development of instruments for investigation in which multiple reflections exist and the use of methods of getting absolute measurement of visibility make it desirable that all these formulas should be reconsidered. Further since x-ray spectra are in general formed from numerous series of multiple reflections from a large number of parallel planes it is important that visibility expressions should also be obtained for transmitted and reflected x-radiation. The Lummer and Gehrcke and the Fabry and Perot interferometers are typical instruments where multiple reflections exist and will serve the purpose of illustration. These instruments may have their reflecting surfaces silvered or clear.

The following notation will be used: I_0 is the intensity of the incident light; $\partial = 4\pi D/\lambda$ where $2D$ is the path difference between two successive rays and λ is the wave-length; p is the number of reflections; b and e are the reflection coefficients and c and f are the transmission coefficients at the two reflecting surfaces, respectively.

The expressions for the intensity are as follows:

1. For silvered plates; (a) with transmitted light

$$I = I_0 \frac{(1-b^{2p})^2 + 4b^{2p}\sin^2(p\partial/2)c^2f^2}{1-2b^2\cos\partial + b^4} \tag{11}$$

which becomes simplified, when p is large to

$$I = I_0 \frac{c^2f^2}{1-2b^2\cos\partial + b^4} \tag{12}$$

(b) with reflected light and p large

$$I = I_0\left[b^2 + \frac{2bcfe(\cos\partial - e^2) + c^2f^2e^2}{1-2e^2\cos\partial + e^4}\right] \tag{13}$$

2. For unsilvered plates where the principle of reversibility may be assumed to hold if the angle of incidence is suitable and consequently $b = -e$ and $1 - b^2 = cf$;

(a) with transmitted light

$$I = I_0 \frac{(1-b^2)^2[(1-b^{2p})^2 + 4b^{2p}\sin^2(p\partial/2)]}{1-2b^2\cos\partial + b^4} \tag{14}$$

(b) with reflected light

$$I = I_0 - \text{expression (14)} \tag{15}$$

these also may become simplified obviously if p is large. Eq. (12) may be taken as the result applicable to the Fabry and Perot interferometer if a monochromatic source emitting radiation of wave-length λ is used. Eqs. (14) and (15) represent the result obtained for the Lummer and Gehrcke plate where $\partial = \mu 4\pi D/\lambda$ in which μ is the index of refraction of the plate.

As in the case of the simple interferometer, if the source is complex (12) becomes

$$I = \int_{-x}^{x} F(x) \frac{c^2 f^2}{1 - 2b^2 \cos \partial + b^4} dx \tag{16}$$

where $\partial = 4\pi D(\overline{m} + x)$, and may be written in the form

$$I \doteq I_0 \frac{c^2 f^2}{1 - b^4} \int_{-x}^{x} F(x)(1 + 2b^2 \cos \partial + 2b^4 \cos 2\partial + \cdot \cdot \cdot) dx \tag{17}$$

In the same way (12) may be written

$$I = I_0 \frac{c^2 f^2}{1 - b^4} (1 + 2b^2 \cos \partial + 2b^4 \cos 2\partial + \cdot \cdot \cdot) \tag{18}$$

and if $2b^4 \cos 2\partial + 2b^6 \cos 3\partial + \cdots$ may be neglected, then in (18)

$$I \doteqdot I_0 \frac{c^2 f^2}{1 - b^4} (1 + 2b^2 \cos \partial) \tag{19}$$

and in (17)

$$I \doteqdot \int_{-x}^{x} \frac{c^2 f^2}{1 - b^4} F(x)(1 + 2b^2 \cos \partial) dx \tag{20}$$

and maximum and minimum intensities are given by

$$I = \frac{c^2 f^2}{1 - b^4} (P \pm 2b^2 \sqrt{C^2 + S^2})$$

where $P = \int F(x) dx$, $C = \int F(x) \cos 4\pi Dx \, dx$, and $S = \int F(x) \sin 4\pi Dx \, dx$ and since $S = 0$ for a symmetrical source

$$I_{max} = \frac{c^2 f^2}{1 - b^4} (P + 2b^2 C) \text{ and } I_{min} = \frac{c^2 f^2}{1 - b^4} (P - 2b^2 C)$$

and therefore

$$V=2b^2C/P=2b^2\exp\left[-(2D)^2\pi^2/h^2\right]. \qquad (21)$$

Using Michelson's form of expression

$$V=2b^2\exp\left[-(2D)^2\pi^2\bar{a}^2/4\log 2\right] \qquad (22)$$

and Rayleigh's form of expression

$$V=2b^2\exp\left[-\pi(\pi\Delta v/\lambda c)^2\right] \qquad (23)$$

an expression which was obtained by Saha[1] and by A. J. Dempster[2] by somewhat different developments.

It may be observed that by increasing b^2 a large path difference Δ may be used and the visibility will persist, for from (23)

$$\Delta=\frac{\lambda c}{\pi v}\sqrt{\frac{1}{\pi}\log\left(2b^2/V\right)} \qquad (24)$$

High values of b^2 may be obtained by the use of reflection at air-metal surfaces, e. g. by silvering the plates in the Fabry and Perot and Lummer and Gehrcke interferometers. Since, however, if b^2 is high, absorption is correspondingly great, the transmitted light may be so weak as to preclude the observation of fringes unless the source is made correspondingly bright. Now however, as b^2 becomes large it is necessary to determine if the approximate formula (19) may be used for (18) and obtain a measure of the error introduced thereby.

Examples may be taken showing the magnitude of the error in the expression for the intensity introduced by the use of $(1+2b^2\cos\partial)$ for $(1-b^4)/(1-2b^2\cos\partial+b^4)$. If $b^2=0.8$ and ∂ be given values successively such that $\cos\partial=1,\ 1/2b^2,\ 0.5,\ 0,\ -0.5,\ -1/2b^2$, it will be seen that there are errors of excess and deficiency that are of very considerable magnitude indeed.

The maxima of the fractional excess and deficiency errors may be shown to occur when $\cos\partial=1$ or $\cos\partial=b^2/4$. In the first case the error is

$$I_0\frac{c^2f^2}{1-b^4}\left(\frac{2b^4}{1-b^2}\right)$$

and the fractional error is $2b^4/(1-b^2)$. If $b^2=0.8$ the fractional error is 0.71. In a similar manner it may be shown that if $\cos\partial=b^2/4$ the fractional error, when $b^2=0.8$, is 3.8.

The error in the expression for the intensity will be zero if $\cos\partial=(b^2\pm\sqrt{b^4+8})/4$ unless at the same time $\cos\partial=(1+b^4)/2b^2$, in which

[1] Saha, Phys. Rev. **10,** 782 (1917)

[2] Dempster, Ann. d. Physik, **47,** 791 (1915).

case $b^2=1$. But b^2 is always less than 1 so that it is possible to find a value for ∂ for which the use of the approximate formulas under consideration is justified.

The error introduced in the expression for the visibility by the substitution of (20) for (17) may also be determined. If (19) be used for intensity the expression for visibility is given by Eq. (21). If (17) is used, then

$$I=\frac{c^2f^2}{1-b^4}(P+2b^2C\cos\theta+2b^4C_1\cos 2\theta+2b^6C_2\cos 3\theta+\cdot\cdot\cdot)$$

where P and C have the same significance as before, $\theta=4\pi Dm$, and

$$C_1=\int_{-x}^{x}F(x)\cos 8\pi Dx\,dx\ ,\quad \text{etc.}$$

Maxima exist where $\theta=2\pi$, 4π, etc., and minima where $\theta=\pi$, 3π, etc. The visibility is therefore given by

$$V=\frac{I_{max}-I_{min}}{I_{max}+I_{min}}=\frac{2b^2C+2b^6C_2+2b^{10}C_4+\cdot\cdot\cdot}{P+2b^4C_1+2b^8C_3+\cdot\cdot\cdot}\doteqdot\frac{2b^2C}{P(1+2b^4C_1/P)}$$

and if it is assumed that $F(x)$ is $\exp[-h^2x^2]$

$$V=\frac{2b^2C}{P\Big(1+2b^4\exp\left[-(4\pi D/h)^2\right]\Big)} \tag{25}$$

Now for low values of $2D$, $\exp[-(4\pi D/h)^2]\doteqdot 1$. It is therefore only when b^2 is a small fraction that (21) may be used to represent visibility in spectra of low order. If one obtains the ratio of the visibilities for two values of $2D$, as was done by Michelson, using, however, values of some magnitude well separated but well towards the limit of visibility, the error which is introduced by the use of (21) for (25) is greatly reduced. It is therefore evident that in the use of formula (21) for visibility and the formulas (22), (23) and (24) which are derived from (21) if the value of V is obtained by means of a silvered Fabry and Perot interferometer or any multiple reflecting instrument where the coefficient of reflection of the intensity is high that errors of some magnitude will appear in the results unless measurements are made where suitable path differences exist.

It should be observed also that the expressions for I_{max} and I_{min} were obtained by neglecting varitions of I with C and S. These were in general negligible for very narrow sources even for small differences in path. But for large differences in path they become quite important. However where visibility is measured near the limit, i. e. for very high values of $2D$, the variations in intensity will have both deficiency and excess values depending on $\cos 4\pi Dx$ and $\sin 4\pi Dx$ and the resultant integrated variation of I with C and S will be negligible.

From (6) and (24) it is clear that the path difference for any assigned value of the visibility is $\sqrt{1-\log 2b^2/\log V}$ times that for the same value of the visibility where multiple reflections do not exist. An increase or decrease exists according as b^2 is greater or lesser than .5. Further if .025 be taken as the limiting value of V the path difference corresponding to this value may be shown from (24) to be of the order of 4 cms. Path differences for the limiting visibility much larger than this are observable experimentally. In fact Fabry[3] obtained visible fringes for a path difference of 43 cm. and Lummer and Gehrcke are credited by H. A. Lorentz[4] with using path differences of over one meter. In these cases the sources which were used emitted intensely bright light.

In the interferometers of Fabry and Perot if the surfaces are not silvered and the light is incident normally $b^2 \doteq 0.05$ i. e. comparatively low. The maximal excess and deficiency errors in the use of the approximate expression for intensity are negligibly small and $V=2b^2C/P$ represents the visibility fairly well even for small path differences. In the interferometer of Lummer and Gehrcke the angle of incidence is very great and b^2 is very high even if the plate is unsilvered. If $i=85°$ $b^2>0.6$ and becomes larger rapidly as the angle of incidence increases and the errors which are associated with the intensity formula are of considerable magnitude. For a fairly thick plate the path difference is large and the expression for visibility is sufficiently accurate. Since, however, only a few orders of spectral fringes appear, it may be necessary to use two plates of the same glass but of different thicknesses in order to get the ratio of the visibilities for two suitable values of the path difference.

If interference is obtained by reflected light and $c^2f^2=(1-b^2)$ the expression for the intensity

$$I=I_0\left[1-\frac{(1-b^2)^2}{1-2b^2\cos\partial+b^4}\right]=I_0\left[\frac{2b^2(1-\cos\partial)}{1-2b^2\cos\partial+b^4}\right]$$

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[3] Fabry, Comptes Rendus **128,** 1223 (1899).
[4] H. A. Lorentz, Phys. Zeits. **11,** 349 (1910).

Therefore

$$I=I_0\left[\frac{2b^2}{1-b^4}(1-\cos\partial)(1+2b^2\cos\partial+2b^4\cos 2\partial+++)\right]$$

and proceeding as in the case for transmitted light, $V=(1-b^2)C/P$.

The intensity formula for use with the Lummer and Gehrcke plate for transmitted light is more accurately that given in (14) which may be written

$$I=I_0\frac{(1-b^2)^2}{1-b^4}\left[(1-2b^{2p}\cos\partial+b^{4p})(1+2b^2\cos\partial+2b^4\cos 2\partial+)\right]$$

If the source has "width" the expression for visibility reduces to (21) if b is small and p is large. Similarly for reflected light

$$I=I_0\left[1-\frac{(1-b^2)^2}{1-b^4}\{(1-2b^{2p}\cos\partial+b^{4p})(1+2b^2\cos\partial+2b^4\cos 2\partial+++)\}\right]$$

and if b is small and p is large $V=(1-b^2)C/P$.

In the development of formulas (21) and (24) no account was taken of absorption between the planes of reflection or of loss by diffuse reflection or scattering. These factors may be ignored if the interferometers are used for the measurement of wave-lengths or for the direct observation of resolved spectral components. If, however, the visibility method is to be employed to determine the character of the source these should be taken into account. If a is the coefficient or loss of amplitude due to these causes the visibility formula (21) becomes

$$V=2b^2(1-a)^2C/P$$

With this modification of (21) formula (24) would become

$$v=\frac{\lambda c}{\pi\Delta}\sqrt{\frac{1}{\pi m}\log\frac{2b^2(1-a)^2}{V}} \qquad (26)$$

if the atomic mass of the source is taken into consideration. Here a is the coefficient of loss of amplitude of the light for one passage of the light through the interferometer plate. Since the length of this path is given by $l=d/\cos\psi$ where d is the thickness of the plate and ψ is the angle of refraction or $l=\mu d/\sqrt{\mu^2-\sin^2 i}$ where μ is the index of refraction of the plate, it is seen that a varies with the angle of incidence. In the case of glass the values of both a and b are accurately known. From (26) the relationship between v and m may be obtained even for close components of spectral lines, since these components may first be obtained by the use of auxiliary spectroscopes of high resolving power.

If the definition of visibility chosen by the late Lord Rayleigh be used in connection with multiple reflection interferometers, viz., $V = I_{min}/I_{max}$ then the considerations of errors which are introduced by the use of the approximate formula above are still applicable. With this definition

$$V = (P - 2b^2C)/(P + 2b^2C)$$

$$= \frac{1 - 2b^2 \exp\left[-(2D)^2\pi^2\bar{a}^2/4 \log 2\right]}{1 + 2b^2 \exp\left[-(2D)^2\pi^2\bar{a}^2/4 \log 2\right]}$$

replaces (16) for transmitted light.

Or in terms of the velocity of the source

$$V = \frac{1 - 2b^2 \exp\left[-\pi(\pi\Delta v/\lambda c)^2\right]}{1 + 2b^2 \exp\left[-\pi(\pi\Delta v/\lambda c)^2\right]}$$

or where absorption is taken into account

$$V = \frac{1 - 2b^2(1-a)^2 \exp\left[-\pi(\pi\Delta v/\lambda c)^2\right]}{1 + 2b^2(1-a)^2 \exp\left[-\pi(\pi\Delta v/\lambda c)^2\right]}$$

which replaces (17).

The Lummer and Gehrcke plate offers some advantages for use with this method of analysis of a source of light.

(1) The angle of incidence is perfectly definite and the coefficients of reflection of intensity of light for air-glass surface at all angles of incidence are shown to a high degree of accuracy.

(2) The group of fringes obtained is for large differences of path and by choice of plates of suitable thickness groups of fringes with well graded visibility may be obtained and measurements may be made at many points suitable for obtaining an accurate visibility curve from which to deduce the conditions in the source.

(3) The plate may be crossed with another plate, with an echelon, or with other spectroscopes and visibility curves for the resolved components thereby obtained. Where components are not resolved they will make themselves evident by a periodic condition in the visibility curve for the fringes of the resolved components.

(4) To obtain measurements of the visibility experimentally fairly accurate results may be obtained from a photograph of the fringes if a uniform beam of light is sent through the photographic plate and the intensity measured for an unaffected part of the plate as well as for the various parts of the plate on which the fringes show. This may be

sufficiently accurate since it is the $\sqrt{\log(1/V)}$ which appears in the formulas (24) and (26). However, a greater degree of accuracy will probably be obtained by the use of a thermocouple, a photoelectric cell or a selenium or thalofide cell to measure the intensities at the maxima and minima.

(5) The existence of wide minima and narrow maxima of the transmitted light presents an opportunity of obtaining greater accuracy in the measurement of visibility than is the case with the simple interferometer since owing to the width of the minima they are not difficult to locate. Moreover, since I_{max} and I_{min} are small quantities, especially for large differences in path, it is imperative that the minima should be located very accurately if the measurement of I_{min} is to be at all accurate.

For a homogeneous source like that which gives the cadmium red line the visibility curve is simple and is obtainable with accuracy by the Michelson interferometer and may be readily interpreted.

For sources of more complex structure, e. g. those of hygroden and helium spectra, it is desirable not only to resolve the fine components but also to obtain the distribution of intensity in these components. Moreover it is now highly desirable to study the Zeeman and Stark effects not only in the production of components but also on the distribution of intensity in the components for use in the elucidation of spectral series and also for the determination of the character of the source. In this work multiple reflection interferometers should be of considerable assistance.

In the spectra of x-rays which are obtained from analyzing crystals of simple form only the first four or five orders are obtainable. Since, however, both the coefficients of absorption a and of reflection b are of very small magnitude, it is possible to develop expressions for intensity and visibility which may be reasonably accurate in these low orders and which may serve to compare crystal formations and perhaps give some information on the character of the source. In this connection there has been a very extensive consideration of the intensity of radiation from imperfect crystals by C. G. Darwin[5] and expressions for the intensity of the maxima for ideally monochromatic radiation when simple and almost perfect crystals are used have been obtained by K. W. Lamson.[6]

TORONTO,
August 5, 1925.

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[5] C. G. Darwin, Phil. Mag. **43,** 800 (1922).

[6] K. W. Lawson, Phys. Rev. **17,** 624 (May, 1921).

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THE RADIATION OF ENERGY AND ANGULAR MOMENTUM

By H. Bateman

Abstract

When an electromagnetic field, derived from retarded potentials, is given it is generally possible to add to this a scalar field, derived from a retarded potential ψ, in such a way that the total radiation of energy to infinity is zero for each direction, the contribution of the scalar field being calculated with the aid of a tensor used in a former paper. The radiation of angular momentum to infinity is not zero for each direction unless the electromagnetic field is of a certain type. The approximate values of the field vectors at a great distance from the origin can be expressed in terms of a quantity α and when the field is of the type just mentioned α satisfies a certain partial differential equation. This result may be regarded as typical for attempts to solve the radiation problem in which the electromagnetic radiation in one of Bohr's stationary states is supposed to be balanced by radiation of a new type. Some remarks are made on the attempts which have been made to solve the problem with the aid of electromagnetic fields alone and a brief discussion is given of the radiation of angular momentum according to the classical theory.

Introduction

1. In a former paper[1] an attempt was made to justify the hypothesis of non-radiating electronic orbits by a modification of electromagnetic theory in which a scalar field, specified by a retarded potential ψ, is supposed to be associated with the ordinary electromagnetic field. It was found that in the periodic motion of a point-electron round a stationary nucleus the radiation to infinity of energy, linear momentum and angular momentum was such that when an average was taken for all directions and for a complete period, the average radiation was in each case zero. Unfortunately, this was not true for each direction and so the result was to some extent unsatisfactory. Attempts to modify the stress-energy tensor with a view to remedying this defect have so far proved unsuccessful[2] and so an attempt will now be made to alter the fields. Some alteration is, indeed, necessary, because, strictly, we are not entitled to represent an electron as a point charge. Moreover, as soon as the electron is treated as of finite size the question of the rate of spin becomes important, not only because the electron, when spinning, acts as a magnetic doublet, but also because a spin will undoubtedly alter the value of ψ.

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[1] H. Bateman, Phys. Rev. **20**, 243 (1922).

[2] H. Bateman, Mess. of Math. **52**, 116 (1922); **53**, 145 (1924); **54**, 142 (1925); M. Salkover, Phys. Rev. **27**, 87 (1926).

Since the rotation and deformation of the electron are unknown we shall assume that the fields are unknown except in so far as they can be represented by retarded potentials of a certain type and shall look for the restrictions, if any, which must be laid on the electromagnetic field in order that there may be no radiation of energy and angular momentum to infinity in any direction.

THE RADIATION OF ENERGY

2. The expressions suggested originally for the components of the tensor giving the distribution of energy and momentum and also their rates of flow were subsequently modified in order that the space outside an isolated stationary electron might be entirely free from stress. The components that have now been adopted[3] for the space outside all the electric charges are of types

$$X_x=\frac{1}{3}(E_x^2+H_x^2)-\frac{1}{6}(E^2+H^2)+\frac{2}{3}\left(\frac{\partial\psi}{\partial x}\right)^2-\frac{k}{8}\frac{\partial^2}{\partial x^2}(\psi^2)-\frac{4-3k}{12}\Gamma\ ,$$

$$X_y=\frac{1}{3}(E_xE_y+H_xH_y)+\frac{2}{3}\frac{\partial\psi}{\partial x}\frac{\partial\psi}{\partial y}-\frac{k}{8}\frac{\partial^2}{\partial x\partial y}(\psi^2)=Y_x\ ,$$

$$W=\frac{1}{6}(E^2+H^2)-\frac{2}{3c^2}\left(\frac{\partial\psi}{\partial t}\right)^2+\frac{k}{8c^2}\frac{\partial^2}{\partial t^2}(\psi^2)-\frac{4-3k}{12}\Gamma\ ,$$

$$S_x=\frac{1}{3}c(E_yH_z-E_zH_y)+\frac{2}{3}\frac{\partial\psi}{\partial x}\frac{\partial\psi}{\partial t}-\frac{k}{8}\frac{\partial^2}{\partial x\partial t}(\psi^2)=c^2G_x\ ,$$

where

$$\Gamma=\left(\frac{\partial\psi}{\partial x}\right)^2+\left(\frac{\partial\psi}{\partial y}\right)^2+\left(\frac{\partial\psi}{\partial z}\right)^2-\frac{1}{c^2}\left(\frac{\partial\psi}{\partial t}\right)^2$$

and $k=1$. If ψ satisfies the wave equation

$$\Box\psi\equiv\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}-\frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2}=0\ ,$$

and the field vectors **E** and **H** satisfy Maxwell's equations

$$\operatorname{curl}\mathbf{H}=\frac{1}{c}\frac{\partial\mathbf{E}}{\partial t}\ ,\qquad \operatorname{div}\mathbf{E}=0$$

$$\operatorname{curl}\mathbf{E}=-\frac{1}{c}\frac{\partial\mathbf{H}}{\partial t}\ ,\qquad \operatorname{div}\mathbf{H}=0$$

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[3] H. Bateman, Phil. Mag. **49**, 1 (1925). With these components the flow of energy in the field of an electron, which is moving uniformly, is at each point parallel to the line of motion of the electron. In the original paper we used the value $k=8/3$.

we have for any constant value of k

$$\frac{\partial X_x}{\partial x}+\frac{\partial X_y}{\partial y}+\frac{\partial X_z}{\partial z}-\frac{\partial G_x}{\partial t}=0\ ,$$

$$\cdots\cdots\cdots\cdots\cdots$$

$$\frac{\partial S_x}{\partial x}+\frac{\partial S_y}{\partial y}+\frac{\partial S_z}{\partial z}+\frac{\partial W}{\partial t}=0\ .$$

Consequently if W represents the density of energy, S_x, S_y, S_z the components of the flow of energy, X_x, X_y, X_z, $\cdots$ the component stresses and G_x, G_y, G_z the densities of the components of linear momentum, we have conservation of energy and linear momentum in any finite portion of free space provided the flux across the boundary of the region is taken into consideration.

3. At a very great distance r from the center of an atom, which we take as our origin, the electromagnetic field may be written in the form

$$\mathbf{H}=-\frac{1}{c}\frac{\partial}{\partial t}\text{ curl }\mathbf{Q}+\text{ curl curl }\mathbf{P}\ ,\quad \mathbf{E}=-\frac{1}{c}\frac{\partial}{\partial t}\text{ curl }\mathbf{P}-\text{ curl curl }\mathbf{Q}$$

where the vectors $\mathbf{Q}$ and $\mathbf{P}$ are given by the series

$$\mathbf{Q}=\frac{\mathbf{q}}{r}+\frac{\partial}{\partial x}\left(\frac{\mathbf{q}_1}{r}\right)+\frac{\partial}{\partial y}\left(\frac{\mathbf{q}_2}{r}\right)+\frac{\partial}{\partial z}\left(\frac{\mathbf{q}_3}{r}\right)+\frac{\partial^2}{\partial x^2}\left(\frac{\mathbf{q}_{11}}{r}\right)+\cdots$$
$$+2\frac{\partial^2}{\partial y\partial z}\left(\frac{\mathbf{q}_{23}}{r}\right)+\cdots$$

$$\mathbf{P}=\frac{\mathbf{p}}{r}+\frac{\partial}{\partial x}\left(\frac{\mathbf{p}_1}{r}\right)+\frac{\partial}{\partial y}\left(\frac{\mathbf{p}_2}{r}\right)+\frac{\partial}{\partial z}\left(\frac{\mathbf{p}_3}{r}\right)+\frac{\partial^2}{\partial x^2}\left(\frac{\mathbf{p}_{11}}{r}\right)+\cdots$$
$$+2\frac{\partial^2}{\partial y\partial z}\left(\frac{\mathbf{p}_{23}}{r}\right)+\cdots\ .$$

in which quantities $\mathbf{q}$, $\mathbf{q}_1$, $\mathbf{q}_2$, $\mathbf{q}_3$, $\mathbf{q}_{11}$, $\cdots$ $\mathbf{p}$, $\mathbf{p}_1$, $\mathbf{p}_2$, $\mathbf{p}_3$, $\mathbf{p}_{11}$, $\cdots$ are all functions of $\tau=t-r/c$. These quantities are supposed to be finite for all values of τ and their derivatives with respect to τ are supposed to be likewise finite. We shall imagine them to be simple trigonometrical functions but this restriction is not necessary. Since these quantities are all bounded we shall disregard them or treat them as constants in estimating the order of magnitude of an expression.

In calculating the radiation of energy and linear momentum we need only retain terms of order $1/r$ in the expressions for $\mathbf{E}$, $\mathbf{H}$ and ψ. Consequently, to this order we may write

$$\mathbf{H}=\mathbf{s}\times\mathbf{b}+\mathbf{s}\times(\mathbf{s}\times\mathbf{a})\ ,\qquad \mathbf{E}=-(\mathbf{s}\times\mathbf{H})$$

where $\mathbf{s}$ is the unit vector with components $(x/r,\ y/r,\ z/r)$ and where

$$\mathbf{a}=\frac{1}{c^2r}\,\mathbf{p}''-\frac{1}{c^3r^2}(x\mathbf{p}_1'''+y\mathbf{p}_2'''+z\mathbf{p}_3''')+\cdots$$

$$\mathbf{b}=\frac{1}{c^2r}\,\mathbf{q}''-\frac{1}{c^3r^2}(x\mathbf{q}_1'''+y\mathbf{q}_2'''+z\mathbf{q}_3''')+\cdots$$

In these equations primes denote differentiations with respect to the argument $t-r/c$. The approximate expressions for $\mathbf{E}$ and $\mathbf{H}$ give

$$\mathbf{E}\times\mathbf{H}=\mathbf{s}[\mathbf{a}^2+\mathbf{b}^2-(\mathbf{a}\cdot\mathbf{s})^2-(\mathbf{b}\cdot\mathbf{s})^2+2\mathbf{s}\cdot(\mathbf{a}\times\mathbf{b})]$$

Assuming that

$$\begin{aligned}\psi&=\frac{\kappa}{r}+\frac{\partial}{\partial x}\left(\frac{\kappa_1}{r}\right)+\frac{\partial}{\partial y}\left(\frac{\kappa_2}{r}\right)+\frac{\partial}{\partial z}\left(\frac{\kappa_3}{r}\right)+\cdots\\&=\frac{\kappa}{r}-\frac{1}{cr^2}(x\kappa_1'+y\kappa_2'+z\kappa_3')+\cdots\end{aligned}$$

approximately, we find that the flow of energy in the direction of $\mathbf{s}$ is $\mathbf{S}$ where

$$\begin{aligned}\mathbf{S}&=\frac{1}{3}\,c(\mathbf{E}\times\mathbf{H})+\frac{2}{3}\,\nabla\psi\frac{\partial\psi}{\partial t}-\frac{k}{4}\,\nabla\psi\frac{\partial\psi}{\partial t}-\frac{k}{4}\,\psi\,\nabla\frac{\partial\psi}{\partial t}\\&=\frac{1}{3}c\mathbf{s}\Big[\mathbf{a}^2+\mathbf{b}^2-(\mathbf{a}\cdot\mathbf{s})^2-(\mathbf{b}\cdot\mathbf{s})^2+2\mathbf{s}\cdot(\mathbf{a}\times\mathbf{b})\\&\qquad-\left(2-\frac{3k}{4}\right)\frac{1}{c^2}\left(\frac{\partial\psi}{\partial t}\right)^2+\frac{3k}{4c^2}\,\psi\,\frac{\partial^2\psi}{\partial t^2}\Big]\end{aligned}$$

approximately. Now ψ can generally be chosen so that this expression vanishes. This is evidently possible when $k=0$ for then we have simply to choose ψ so that $(\partial\psi/\partial\tau)^2$ is a given positive function. When $k\neq 0$ we have to solve an equation of type

$$\begin{aligned}\left(2-\frac{3k}{4}\right)\left(\frac{\partial\psi}{\partial\tau}\right)^2-\frac{3k}{4}\,\psi\,\frac{\partial^2\psi}{\partial\tau^2}&=\frac{1}{r^2}\left[f\left(\frac{x}{r},\frac{y}{r},\frac{z}{r},\tau\right)\right]^2\\&=[F(\tau)]^2\ \text{say}.\end{aligned}$$

It seems likely that a solution exists only when $F(\tau)$ is subject to certain restrictions. A general existence theorem for this differential equation is hard to find but it is easy to see that there are many cases in which the equation possesses a real solution. To see this let us put

$$\psi=e^\sigma\ ,\qquad F(\tau)=e^\sigma G(\tau)$$

When σ is given we can find F if it is possible to choose a real function G such that

$$\left(2-\frac{3k}{2}\right)\left(\frac{\partial\sigma}{\partial\tau}\right)^2-\frac{3k}{4}\frac{\partial^2\sigma}{\partial\tau^2}=[G(\tau)]^2 \tag{1}$$

The quantity on the left-hand side must thus be positive. Let us now alter the problem a little and endeavor to determine σ when G is given. We then have to solve a Riccatian equation

$$\left(2-\frac{3k}{2}\right)\rho^2-\frac{3k}{4}\frac{\partial\rho}{\partial\tau}=[G](\tau)^2$$

for $\rho=\partial\sigma/\partial\tau$. Putting

$$\rho=-\frac{3k}{8-6k}\cdot\frac{1}{u}\frac{du}{d\tau}$$

we have the linear differential equation

$$\frac{d^2u}{d\tau^2}=\frac{8u}{9k^2}(4-3k)[G(\tau)]^2$$

for the determination of u and this equation generally possesses a real solution when $G(\tau)$ is an analytic function. Since $G(\tau)$ is practically arbitrary the function $F(\tau)$ is also of a very general nature. The restriction which is introduced by the circumstance that $F(\tau)=e^\sigma G(\tau)$, where σ is a solution of (1) does not seem to be very great.

THE RADIATION OF ANGULAR MOMENTUM

3. When the radiation of energy is zero for each direction the radiation of linear momentum is also zero for each direction since the components of linear momentum are proportional to the components of the flow of energy and the momentum travels in a radial direction.

The rate of flow in a radial direction of the z-component of angular momentum is

$$-\frac{1}{r}[x(xY_x-yX_x)+y(xY_y-yX_y)+z(xY_z-yX_z)]\ .$$

This will be zero for each direction if

$$E_r(xE_y-yE_x)+H_r(xH_y-yH_x)+\left(2-\frac{3}{4}k\right)\frac{\partial\psi}{\partial r}\left(x\frac{\partial\psi}{\partial y}-y\frac{\partial\psi}{\partial x}\right)$$
$$-\psi\frac{3k}{4r}\left(x\frac{\partial}{\partial x}+y\frac{\partial}{\partial y}+z\frac{\partial}{\partial z}-1\right)\left(x\frac{\partial\psi}{\partial y}-y\frac{\partial\psi}{\partial x}\right)=0\ ,$$

where the suffix r is used to denote the radial component. Introducing the polar coordinates

$$z = r\cos\theta\ , \qquad x = r\sin\theta\cos\phi\ , \qquad y = r\sin\theta\sin\phi\ ,$$

we may write

$$x\frac{\partial\psi}{\partial y} - y\frac{\partial\psi}{\partial x} = \frac{\partial\psi}{\partial\phi}\ ,$$

$$x\left(z\frac{\partial\psi}{\partial x} - x\frac{\partial\psi}{\partial z}\right) - y\left(y\frac{\partial\psi}{\partial z} - z\frac{\partial\psi}{\partial y}\right) = r\sin\theta\frac{\partial\psi}{\partial\theta}\ .$$

So far as terms of order $1/r$ are concerned we may also write

$$\frac{\partial\psi}{\partial r} = -\frac{1}{c}\frac{\partial\psi}{\partial\tau}$$

Now E_r and H_r are both of order $1/r^2$ consequently we may retain only terms of order $1/r$ in calculating $(xE_y - yE_x)/r$ and $(xH_y - yH_x)/r$. In particular we may write

$$xE_y - yE_x = rH_z\ , \qquad xH_y - yH_x = -rE_z$$

$$x(zE_x - xE_z) - y(yE_z - zE_y) = z(xE_x + yE_y + zE_z) - r^2E_z$$

$$= -r^2E_z$$

$$x(zH_x - xH_z) - y(yH_z - zH_y) = -r^2H_z$$

Writing

$$H_z = -H_\theta\sin\theta\ , \qquad E_z = -E_\theta\sin\theta$$

$$H_\theta = E\cos\omega\ , \qquad E_\theta = E\sin\omega$$

$$rH_r = u\cos\omega + v\sin\omega\ , \qquad rE_r = u\sin\omega - v\cos\omega$$

we find that the radiation of energy and angular momentum will be zero for each direction if the following equations are satisfied.

$$E^2 = \left(2 - \frac{3}{4}k\right)\frac{1}{c^2}\left(\frac{\partial\psi}{\partial\tau}\right)^2 - \frac{3}{4c^2}k\psi\frac{\partial^2\psi}{\partial\tau^2}$$

$$Eu = \left(2 - \frac{3}{4}k\right)\frac{1}{c}\frac{\partial\psi}{\partial\theta}\frac{\partial\psi}{\partial\tau} - \frac{3}{4c}k\psi\frac{\partial^2\psi}{\partial\theta\partial\tau} \qquad (2)$$

$$Ev\sin\theta = \left(2 - \frac{3}{4}k\right)\frac{1}{c}\frac{\partial\psi}{\partial\phi}\frac{\partial\psi}{\partial\tau} - \frac{3}{4c}k\psi\frac{\partial^2\psi}{\partial\phi\partial\tau}$$

We shall find it convenient to write

$$2 - \frac{3}{4}k = \lambda\ , \qquad \frac{3}{4}k = \mu\ , \qquad \psi = c\alpha\ .$$

When we take into consideration the fact that each of the quantities E_θ, E_ϕ, H_θ, H_ϕ, rE_r, rH_r is of the form $f(\theta, \phi, \tau)/r$ Maxwell's equations in polar coordinates may be written

$$\frac{1}{c} \sin\theta \frac{\partial}{\partial t}(rE_r) = \frac{\partial}{\partial\theta}(\sin\theta\, H_\phi) - \frac{\partial H_\theta}{\partial\phi}$$

$$\frac{1}{c} \sin\theta \frac{\partial}{\partial t}(rE_\theta) = \frac{\partial H_r}{\partial\phi} - \frac{\partial}{\partial r}(r\sin\theta\, H_\phi) \equiv \frac{1}{c} \sin\theta \frac{\partial}{\partial t}(rH_\phi)$$

$$\frac{1}{c} \frac{\partial}{\partial t}(rE_\phi) = \frac{\partial}{\partial r}(rH_\theta) - \frac{\partial H_r}{\partial\theta} \equiv - \frac{1}{c} \frac{\partial}{\partial t}(rH_\theta)$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

and give simply

$$E_\theta = H_\phi\ , \qquad E_\phi = -H_\theta$$

$$\frac{1}{c} \sin\theta \frac{\partial}{\partial\tau}(rE_r) = \frac{\partial}{\partial\theta}(\sin\theta \cdot E_\theta) - \frac{\partial H_\theta}{\partial\phi}$$

$$\frac{1}{c} \sin\theta \frac{\partial}{\partial\tau}(rH_r) = \frac{\partial}{\partial\theta}(\sin\theta \cdot H_\theta) + \frac{\partial E_\theta}{\partial\phi}$$

Substituting the values of E_θ, H_θ, rE_r, rH_r in terms of u, v, E and ω, we obtain

$$\left.\begin{aligned} \frac{1}{c} \sin\theta \left(\frac{\partial u}{\partial\tau} + v\frac{\partial\omega}{\partial\tau}\right) &= E\cos\theta + \sin\theta \frac{\partial E}{\partial\theta} + E\frac{\partial\omega}{\partial\phi} \\ \frac{1}{c} \sin\theta \left(\frac{\partial v}{\partial\tau} - u\frac{\partial\omega}{\partial\tau}\right) &= \frac{\partial E}{\partial\phi} - E\sin\theta \frac{\partial\omega}{\partial\theta} \end{aligned}\right\} \qquad (3)$$

Writing $\lambda\log\alpha - \mu\log\partial\alpha/\partial\tau = \beta$ and making use of the relations (2) we obtain the following differential equations for ω.

$$\left.\begin{aligned} \frac{1}{\sin\theta} \frac{\partial(\omega,\beta)}{\partial(\phi,\tau)} &= \frac{1}{2} \frac{\partial(\log\partial\beta/\partial\tau, \beta)}{\partial(\theta,\tau)} + \frac{\partial(\log\alpha, \log\partial\alpha/\partial\tau)}{\partial(\theta,\tau)} - \frac{\partial\beta}{\partial\tau}\cot\theta \\ \frac{\partial(\omega,\beta)}{\partial(\theta,\tau)} &= -\frac{1}{\sin\theta}\left[\frac{1}{2} \frac{\partial(\log\partial\beta/\partial\tau, \beta)}{\partial(\phi,\tau)} + \frac{\partial(\log\alpha, \log\partial\alpha/\partial\tau)}{\partial(\phi,\tau)}\right] \end{aligned}\right. \qquad (4)$$

When $k=0$ we have $\beta = 2\log\alpha$ and the equations for ω reduce to

$$\frac{\partial(\omega,\beta)}{\partial(\phi,\tau)} = -\frac{\partial\beta}{\partial\tau}\cos\theta\ , \qquad \frac{\partial(\omega,\beta)}{\partial(\theta,\tau)} = 0\ ,$$

The last equation gives

$$\omega = F(\beta, \phi)\ ,$$

and when we substitute in the first equation we find that

$$\left(\frac{\partial F}{\partial \phi}+\cos\theta\right)\frac{\partial \beta}{\partial \tau}=0.$$

This equation gives a value of β which is independent of τ and so when $k=0$ there is no solution which is of physical interest. When $k\neq 0$ we may eliminate ω from the equations

$$\frac{\partial(\omega,\beta)}{\partial(\phi,\tau)}=\Theta\ , \qquad \frac{\partial(\omega,\beta)}{\partial(\theta,\tau)}=-\Phi \tag{5}$$

and obtain a partial differential equation for α. The result is

$$\Theta\frac{\partial^2\beta}{\partial\theta\,\partial\tau}+\Phi\frac{\partial^2\beta}{\partial\phi\partial\tau}=\frac{\partial\beta}{\partial\tau}\left[\frac{\partial\Theta}{\partial\theta}+\frac{\partial\Phi}{\partial\phi}\right]-\frac{\partial\beta}{\partial\theta}\ \frac{\partial\Theta}{\partial\tau}-\frac{\partial\beta}{\partial\phi}\ \frac{\partial\Phi}{\partial\tau}$$
$$+\frac{\dfrac{\partial^2\beta}{\partial\tau^2}}{\dfrac{\partial\beta}{\partial\tau}}\left[\Theta\frac{\partial\beta}{\partial\theta}-\Phi\frac{\partial\beta}{\partial\phi}\right]$$

where Θ and Φ have the values obtained by substituting (5) in (4). The general solution of this partial differential equation will probably be difficult to obtain. A particular solution may be obtained at once by assuming that α and ω are independent of ϕ. The equations (4) then give

$$\omega=f(\beta)$$

$$\frac{1}{2}\ \frac{\partial(\log\partial\beta/\partial\tau,\beta)}{\partial(\theta,\tau)}+\frac{\partial(\log\alpha,\log(\partial\alpha/\partial\tau)}{\partial(\theta,\tau)}=\frac{\partial\beta}{\partial\tau}\cos\theta$$

In this case the axis of z is an axis of symmetry for the fields and so from the point of view of Bohr's theory of the atom the fields are not of much physical interest.

Further discussion of the differential equation must be postponed until the nature of the solutions is better understood. Another differential equation which is more easily treated is obtained by considering the case in which

$$E^2=\frac{1}{c^2}\ \frac{\partial\Omega}{\partial t}\ , \qquad Eu=\frac{1}{c}\ \frac{\partial\Omega}{\partial\theta}\ , \qquad Eu\sin\theta=\frac{1}{c}\ \frac{\partial\Omega}{\partial\phi}\ .$$

Substituting in equations (3) we find that if $\chi=\log(\operatorname{cosec}^2\theta\cdot\partial\Omega/\partial\tau)$

$$\operatorname{cosec}\theta\frac{\partial(\omega,\Omega)}{\partial(\phi,\tau)}=\frac{1}{2}\frac{\partial(\chi,\Omega)}{\partial(\theta,\tau)}$$

$$\frac{\partial(\omega,\Omega)}{\partial(\theta,\tau)}=-\frac{1}{2}\operatorname{cosec}\theta\frac{\partial(\chi,\Omega)}{\partial(\phi,\tau)}$$

Writing

$$\omega+\frac{1}{2}i\log\left(\frac{\partial\Omega}{\partial\tau}\operatorname{cosec}^2\theta\right)=\alpha\ ,\qquad \omega-i\chi=\beta$$

$$\sigma=\log\tan\frac{1}{2}\theta+i\phi\ ,\qquad \rho=\log\tan\frac{1}{2}\theta-i\phi$$

we have

$$\frac{\partial(\alpha,\Omega)}{\partial(\sigma,\tau)}=0\ ,\qquad \frac{\partial(\beta,\Omega)}{\partial(\rho,\tau)}=0\ ,$$

These equations are satisfied by

$$\alpha=i\log f[\Omega,\sigma]$$

$$\beta=-i\log f[\Omega,\rho]$$

where f is an arbitrary function of its two arguments. We finally obtain

$$\partial\Omega/\partial t=\sin^2\theta\, f[\Omega,\log\tan\tfrac{1}{2}\theta+i\phi]f[\Omega,\log\tan\tfrac{1}{2}\theta-i\phi]\ ,$$

This may be regarded as a partial differential equation for the determination of Ω. This partial differential equation may be solved in a large number of cases.

The electromagnetic field determined by a function Ω of this type is particularly interesting because the rate of radiation of energy is a time derivative and so the total radiation in any interval of time may be expressed as the difference of the initial and final values of a certain quantity. The rate of radiation of the z-component of angular momentum may, too, be expressed in a simple form, for in the integral

$$\int_0^\pi\int_0^{2\pi}(\partial\Omega/\partial\phi)\sin\theta\,d\theta\,d\phi$$

the integration with respect to ϕ may be performed at once. If the function Ω is single-valued in ϕ, there is no radiation of this component.

If it ever becomes possible to describe the properties of radiation on the basis of the classical electromagnetic theory alone this type of field may be of some interest.

REMARKS ON THE CLASSICAL THEORY

4. A new attempt to solve the radiation problem on the basis of Maxwell's electromagnetic equations has been made recently by N. v. Raschevsky.[4] His work possesses some good features inasmuch as an attempt is made to find a field which first gives no radiation in a stationary state, then passes over into a state in which there is radiation and finally returns to another stationary state in which there is no radiation. His field which gives no radiation is represented by means of integrals of Kirchhoff's type including surface integrals one of which is practically the potential of a double layer. Now in ordinary potential theory the potential of a double layer is discontinuous at the layer itself. Consequently one is left with the impression that Raschevsky's field is not really a continuous field. This is a defect but may not be a fatal objection to the theory because the discontinuity may simply mean that the ordinary Maxwell field-equations break down in the immediate vicinity of an atom when the fields are very strong. There may be equations something like Maxwell's but the relations

$$\mathbf{D}=\mathbf{E}\ , \qquad \mathbf{B}=\mathbf{H}$$

expressing a simple proportionality between stress and strain may no longer hold. Like the solution proposed by Dr. H. A. Lorentz, in his lectures at Pasadena, Raschevsky's solution has the advantage of giving no radiation in any direction at any instant and since the field vectors are of order $1/r^2$ at a great distance from the origin, there is no radiation of angular momentum.

5. Like most writers Raschevsky takes a vibrating electric dipole as a model of an electromagnetic radiator. The radiation of angular momentum in the field of a dipole has been calculated by several writers[5] and Rubinowicz has used the results to formulate a selection principle in quantum theory.

A point that seems rather puzzling is that when the dipole rotates like a rigid body the angular momentum about the z-axis is radiated not in the direction of the axis, the direction in which the light is circularly polarized, but chiefly in the neighborhood of the plane of rotation and in directions in which the light is linearly polarized. As Ehrenfest pointed out, the theory of the Hertzian dipole gives no support to Poynting's idea that circularly polarized light is accompanied by angular momentum.

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[4] N. v. Raschevsky, Zeits. f. Physik **35**, 100 (1925).

[5] For the literature see W. H. Westphal, Jahrb. d. Radioaktivität. **18**, 105 (1921).

The radiation of angular momentum in the field of the vibrating diplole is seen to depend on the fact that the flow of energy is strictly not in a radial direction and that consequently there is a moment arm from the origin to the line of flow. The length of this perpendicular may be found as follows:

Let us take $\mathbf{P}=0$, $r\mathbf{Q}=\mathbf{q}(t-r/c)$, then, retaining terms of orders $1/r^2$ and $1/r^3$ we have

$$E^2=H^2=\frac{r^2\mathrm{q}''^2-(\mathbf{r}\cdot\mathrm{q}'')^2}{c^4r^4}+2\frac{r^2(\mathrm{q}'\cdot\mathrm{q}'')-(\mathbf{r}\cdot\mathrm{q}')(\mathbf{r}\cdot\mathrm{q}'')}{c^3r^5}$$

$$\mathbf{E}\times\mathbf{H}=\mathbf{s}\left[E^2-\frac{2(\mathbf{r}\cdot\mathrm{q}')(\mathbf{r}\cdot\mathrm{q}'')}{c^3r^5}\right]+\frac{2\mathrm{q}''(\mathbf{r}\cdot\mathrm{q}')}{c^3r^4}$$

Using ϖ to denote the length of the perpendicular from the origin to the line of flow, we have

$$\varpi^2=\frac{[\mathbf{r}\times(\mathbf{E}\times\mathbf{H})]^2}{E^2}=\frac{4(\mathbf{r}\cdot\mathrm{q}')^2}{c^6r^8E^4}[\mathbf{r}^2q''^2-(\mathbf{r}\cdot\mathrm{q}'')^2]$$

Replacing E^2 by its approximate value

$$\frac{1}{c^4r^4}[r^2q''^2-(\mathbf{r}\cdot\mathrm{q}'')$$

we find that

$$\varpi^2=\frac{4c^2(\mathbf{r}\cdot\mathrm{q}')^2}{r^2q''^2-(\mathbf{r}\cdot\mathrm{q}'')^2}$$

When

$$q_x=a\cos 2\pi\nu\tau\ , \qquad q_y=a\sin 2\pi\nu\tau\ , \qquad q_z=0\ ,$$

we have

$$\varpi^2=\frac{c^2}{\pi^2\nu^2}\ \frac{(y\cos 2\pi\nu\tau-x\sin 2\pi\nu\tau)^2}{z^2+(y\cos 2\pi\nu\tau-x\sin 2\pi\nu\tau)^2}$$

This formula indicates that ϖ lies between zero and $c/\pi\nu$; it is zero on the axis of z when $x=y=0$ and has its maximum value in the plane $z=0$.

A line drawn through the point (x, y, z) in the direction of Poynting's vector will, to the present order of approximation, meet the plane of xy in a point whose coordinates are

$$X = J \cos 2\pi\nu\tau \ , \qquad Y = J \sin 2\pi\nu\tau$$

where

$$J = \frac{cr}{\pi\nu} \ \frac{(y \cos 2\pi\nu\tau - x \sin 2\pi\nu\tau)}{z^2 + (y \cos 2\pi\nu\tau - x \sin 2\pi\nu\tau)^2}$$

approximately. Eliminating τ we obtain the equation

$$\frac{\pi\nu z^2}{cr}(X^2+Y^2) + (yX - xY)\left(yX - xY - \frac{cr}{\pi\nu}\right) = 0$$

The lines of motion which pass through the point (x, y, z) thus generate a quadric cone.

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MAY, 1926 PHYSICAL REVIEW VOLUME 27

MEAN INTENSITY OF SOUND IN AN AUDITORIUM AND OPTIMUM REVERBERATION

By Samuel Lifshitz

Abstract

The optimum time of reverberation was determined experimentally for the piano, the violin, the violoncello, for bass and soprano voices and human speech in a room of 260 m^3. The experimental determinations (1.08-1.14 sec.) give the mean value of 1.11 sec. An earlier investigation in a smaller hall of 126 m^3 gave a mean optimum time of $T_{op}=1.06$ sec. It is evident that a mean intensity of sound exists which is the same for human speech and muiscal performances of different kinds, with respect to which our ear determines the optimum of the impression. The value of this intensity (10^{6n} times minimum audible intensity, i) is given by the formula: $1.333n+\log_{10}(aS_1)=3.07$. For $aS_1=49.5$, the mean intensity is equal to $10^{6.019}$. From this, we have as the formula for the optimum time of reverberation, for a room of W m^3 volume:

$$\log_{10}W=8.5+\log_{10}T_{op}-\frac{6.194}{\sqrt[2]{T_{op}}}.$$

Considering the importance of the experimental determination of the optimum time of reverberation, we have verified again, in a different room, the conclusion that the optimum for the same hall is identical for different musical performances and speech.

The investigation was conducted in the concert hall of the State Institute of Musical Science in Moscow. This hall has a volume of 265m^3 and seats 120 persons. The reverberation for the empty hall is 2.63 seconds. During the musical performances, we changed the number of auditors and, by this means, determined the optimum of reverberation. Instead of a piano, we made use of an automatic performer, the so-called "Mignon-piano," so that the music and its performance could be repeated identically for different conditions of the experiment. Results obtained are as follows:

Source	Optimum reverberation
piano	1.13 sec.
violin	1.11 sec.
violoncello	1.11 sec.
bass voice	1.11 sec.
soprano voice	1.11 sec.
human speech[1]	1.14–1.08 sec.
mean (T_{op})	$=1.11$ sec.

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[1] For speech, we determined the optimum when the finest quality of the voice was obtained. Further decreases in the reverberation increased the clearness of speech, but the quality of the voice sounded dry. See V. O. Knudsen, Phys. Rev. **26**, 287 (August, 1925).

Our previous investigations[2] gave a mean value of 1.03 sec. The mean value obtained by Wallace Sabine[3] was 1.08 sec., while a similar value found by Watson[4] was 1.04 sec. The average of all these mean values is 1.06 sec., as found in the previous investigation, and gives the optimum reverberation for music and speech for the investigated small halls with volumes varying from 74 to 260 m^3. We can explain this result if we assume that a constant mean intensity of sound exists for different kinds of music and speech, with respect to which our ear determines the quality of the music heard.

The following considerations give us the meaning of the average acoustic intensity. Let the optimum time (1.06 sec.) hold for a hall of less than W_1 m^3. For smaller halls, the optimum can remain constant because the performer appropriately diminishes the loudness of his voice or musical instrument to suit the conditions of the room. Let the absorption of the hall $W_1 = aS_1$ and the mean intensity of sound be given by $I_1/i = 10^{6n}$ (where i is the threshold intensity and n is variable depending on conditions. For $n=1$, $I_1/i = 10^6$); the actual reverberation therein will be equal to 1.06n sec. In the larger room W_2, with the absorption equal to aS_2, the mean intensity of sound will be less; or $I_2/i = 10^{6n} aS_1/aS_2$. The actual reverberation will be t_2 seconds; the reverberation corresponding to the standard intensity, $I_0/i = 10^6$, will be t_3.

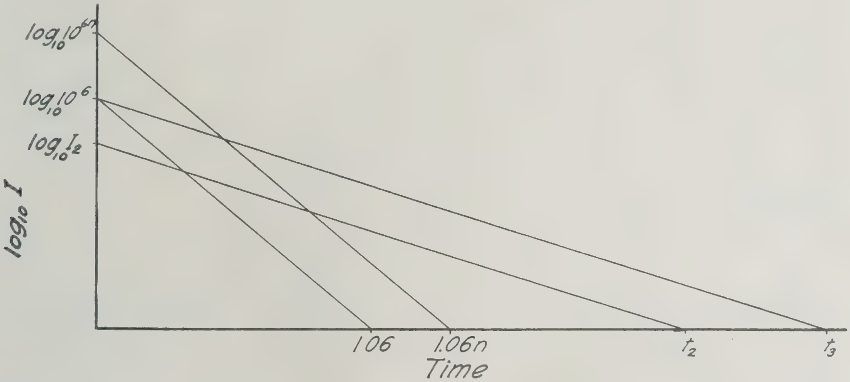

Fig. 1. Showing relative values of t and $\log I$, based on the linear relation, $at = 2.3 \log_{10} (I_0/i)$, derived from the reverberation equation: $i = I_0 e^{-at}$.

If we want to get a good musical impression in a larger room with a smaller intensity of sound, it is assumed necessary to have a longer time of reverberation. That is, the energy of musical perception must be constant, or

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[2] Lifshitz Phys. Rev. **25**, 391 (March, 1925).

[3] Wallace Sabine, "Collected Works," page 75.

[4] F. R. Watson, "Acoustics of Buildings," page 51.

$$t \log_{10} I = \text{constant}. \qquad (1)$$

(The intensity is perceived, according to Weber-Fechner's law, in proportion to its logarithm.)[5]

In our case of the two halls W_1 and W_2, the equation will take the form:

$$t_2 \log_{10} I_2 = 6.36n^2 .$$

From Fig. 1, we have by similar triangles:

$$t_2 : t_3 = \log_{10} I_2 : \log_{10} 10^6$$

or

$$t_2 = t_3 (\log_{10} I_2)/6$$

and on the basis of (1), we can write:

$$t_3^{\frac{1}{2}} \log_{10} I_2 = 6.175n$$

$$\log_{10} I_2 = \log_{10}(10^{6n} aS_1/aS_2) .$$

Substituting we have:

$$t_3^{\frac{1}{2}}[6n + \log_{10}(aS_1) - \log_{10}(aS_2)] = 6.175n. \qquad (2)$$

Let us substitute in the last equation the acoustic data for a perfect hall. As an example of such a hall we can take the Column Hall of the House of Unions in Moscow. This hall has a volume of 12,500 m³.

$$T_{op} = 1.75 \text{ sec.,} \qquad aS_2 = 1175.$$

Then we have:

$$1.333n + \log_{10}(aS_1) = 3.07 \qquad (3)$$

where $aS_1 = .164 W_1/1.06$. Eq. (3) gives the relation between n and the maximum volume W_1 for which the optimum time of reverberation of 1.06 sec. holds. According to our previous supposition, ($n = 1$ for $I = 10^6 i$), the volume $W_1 = 350$ m³.

Paul Sabine[6] takes $\log_{10} I = (9.1 - \log_{10} a)$ in English units, basing this on his experiments on the intensity of the sound of the voice and instruments; from which, according to (3)

$$n = 1.07 ; \qquad W_1 = 285\ m^3 ; \qquad I = 10^{6.42}.$$

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[5] Vern O. Knudsen, Phys. Rev. **21**, 84 (1923).

[6] Paul Sabine. "Acoustics in Auditorium Design," Amer. Archt., June, 1924.

Considering the small difference between Sabine's values and those obtained by the author, we take for the mean volume: $W_1 = 320$ m^3, from which

$$n = 1.0032 \text{ and } I/i = 10^{6.019}.$$

Later, when the optimum time of reverberation is investigated for a larger number of rooms and the determinations made for n and W_1, for which the closest coincidence occurs with experimental results, we shall have more exact values. Substituting our determinations for n and W_1 in the formula (2), we have the equation for the optimum time, T_{op}

$$\log_{10} W = 8.5 + \log_{10} T_{op} - \frac{6.194}{\sqrt{T_{op}}} . \tag{4}$$

This equation is more exact than my previous one,[2] but it differs from it numerically by the amount of experimental errors.

In comparison with the results of my measurements of Russian halls, I give data for some American halls:[4]

	Volume in m^3	Full number of people present	Reverberation of full hall	Optimum according to (4) "perfect acoustics"
1. Munic. Audt.	31000		2.13 sec.	2.05 sec.
2. Gt. Hall, Coll. N. Y.	23400		1.97 sec.	1.96 sec.
3. Eastman Theatre	22400	3340	2.08 sec.	1.95 sec.
4. Boston Music Hall	18300	2471	2.31 sec. (rather loud, 22%)	1.88 sec.
5. Leipzig Gewandhaus	11400	1597	2.30 sec. (rather loud, 35%)	1.73 sec.
6. Detroit Orch. Hall	8350		1.55 sec.	1.65 sec.
7. Smith Concert Hall	6550	1042	1.67 sec.	1.60 sec.
8. Apollo Theatre	5900	1670	1.34 sec. ("dry", perfect for 1235 persons)	1.57 sec.
9. Kilbourn Hall	3960	510	1.65 sec. (satisfactory, rather loud)	1.50 sec.
10. Wesley Auditorium	2860	500	1.16 sec. ("dry", perfect for 300 persons)	1.42 sec.
11. Little Theatre	1730		1.28 sec.	1.32 sec.

THE PHYSICAL INSTITUTE OF THE UNIVERSITY OF MOSCOW,
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ROTATION OF THE PULLEY IN MELDE'S EXPERIMENT

By Arthur Taber Jones

Abstract

The apparently continuous rotation which may sometimes be observed in the pulley in Melde's experiment is assumed to be the result of a succession of small slips of the pulley under the string near some particular phase of the motion. The *equations of motion* are solved under the assumptions that there is no transverse vibration of the string, that the string does not slip on the pulley, that there is no damping, and that the motion is simple harmonic with a frequency equal to that of the tuning fork. It is shown that any slipping will first occur when the pulley is close to an end of its swing, and from this it follows that the sense of a net rotation is determined by the particular end of the swing at which this slipping occurs. The theory indicates that the sense of the rotation depends on the length of the vertical part of the string, but is independent of the length of the horizontal part. In experimental tests of the above theory, the senses of rotation observed for different lengths of the vertical part of the string agree with the theory in a great many cases, but differ in so many other cases as to show that the theory needs modification—probably by taking account of damping. The string used shows considerable elastic after effect, and its *modulus of elasticity* increases with the load. Values of the elastic modulus calculated from the lengths at which the rotation of the pulley reversed show a moderately good agreement with directly determined values. Values of the coefficient of friction between string and pulley, calculated from the amplitude of the pulley when rotation began, are in fair agreement with values which were found directly.

Introduction

In Melde's beautiful experiment[1] a tuning fork sets up standing waves in a string. The string often runs horizontally from the fork to a pulley and then downward to a point where it may be fastened or may carry a small load. Raman and Apparao,[2] A. W. Porter,[3] and J. S. Stokes,[4] independently discovered that the pulley may sometimes appear to rotate continuously. The rotation requires the fork so placed as to set up a longitudinal vibration in the string, but transverse vibration may or may not be present. Stokes found that under certain circumstances a little beeswax applied to the part of the string in contact with the pulley reversed the rotation, and a drop of kerosene in the groove in the pulley restored the original rotation.

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[1] F. Melde, Pogg. Ann. **109,** 192 (1859); **111,** 513 (1860); Wied. Ann. **21,** 452 (1884); **24,** 497 (1885).

[2] C. V. Raman, Phys. Rev. **32,** 307 (1911).

[3] A. W. Porter, Knowledge and Scientific News, **5,** 193 (1908).

[4] J. S. Stokes, Phys. Rev. **30,** 659 (1910).

Shortly after Stokes's discovery I found it possible to reverse the rotation without wax or kerosene. Sometimes forcing a change in the length of the vibrating segment next to the pulley led to a reversal, and sometimes a slight change in the tension of the string sufficed. I also found that if the string passed over two pulleys there might be a rotation of both. This study was very incomplete, and the results were not published. In a joint article[5] several years later I published a few additional facts, and shortly afterward a suggestion[6] as to the general explanation of the rotation. The present paper, restricted to the case where there is no transverse vibration of the string, makes a beginning at a more complete theory of these phenomena, and gives some experimental tests of the theory.

THEORY

Cause of rotation. The explanation of the rotation is doubtless to be found in a slipping between the pulley and the string at some particular phase of the motion. Now when a string is on the point of slipping along a curved surface it is well known that the tensions, T_1 and T_2, in the free ends of the string are connected by the relation

$$T_2 = T_1 e^{\mu\varphi} \,, \tag{1}$$

where μ stands for the coefficient of friction, and φ for the supplement of the angle made by the free parts of the string. If the tensions vary, and the angle between the free parts of the string does not change, the string slips when the ratio of the tensions becomes sufficiently great.

In considering Melde's experiment let us deal only with the case where there is no transverse vibration of the string, and let us for the present assume that the string does not slip on the pulley. Let the tensions (Fig. 1) be given by the equations

$$T_l = T_0 + L \cos pt$$

and

$$T_h = T_0 + H \cos pt \,,$$

and let both L and H be smaller than T_0. Set $L = H + S$. Then

$$T_l / T_h = 1 + S \cos pt / (T_0 + H \cos pt) \,.$$

This ratio attains its extreme values when $pt = 0$ and $pt = \pi$. Moreover, the ratio of the larger tension to the smaller has different values when $pt = 0$ and when $pt = \pi$. These facts mean that when the amplitude of the pulley becomes sufficient for slipping to begin, it begins with the pulley at an end of its swing, and at one end rather than at the other. It follows that there is a succession of small slips, all in one direction, and if the frequency is sufficient this succession of small net rotations looks as if it were one continuous rotation.

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[5] A. T. Jones and M. E. Phelps, Phys. Rev. 10, 544 (1917).

[6] A. T. Jones, Phys. Rev. 11, 150 (1918).

General method of determining sense of rotation. If we examine the various possible cases as to the signs of L, H, and S, we find that the ratio of the larger tension to the smaller is greater at that end of the swing at which the tension which varies most has its smallest value. To determine the sense of the rotation of the pulley we therefore ask first in which part of the string the variation in tension is the greater.

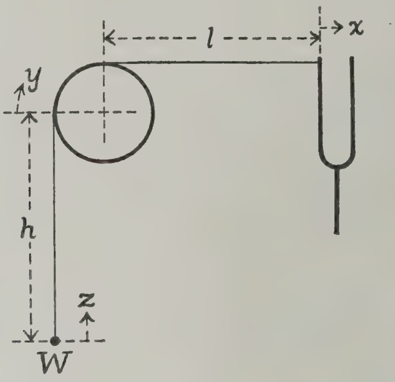

Fig. 1. Meaning of symbols. A rotation in the sense of the arrow y is called ***rotation toward*** the fork, and rotation in the opposite sense is called ***rotation away*** from the fork.

Choosing that part of the string, we then find the position of the pulley when the tension in that part of the string is the least. If this occurs when the pulley is at the end of a swing toward the fork, any slipping will allow it to swing on a little farther toward the fork, and there will be a net of rotation toward the fork. Similar statements apply for rotation away from the fork.

End of string fastened. Let the end of the string at W (Fig. 1) be fastened. Let the amplitude of the pulley be so small that there is no slipping, and consequently no net rotation. To simplify matters let us also neglect damping. Let l and h stand for the lengths of the horizontal and vertical parts of the string, both of them measured when the fork and pulley are in their equilibrium positions, and let l_0 and h_0 stand for the unstretched lengths of these same parts of the string. Let x stand for the displacement of the end of the prong of the fork, and y for the displacement of a point in the groove of the pulley. Then the tensions in the two parts of the string are

$$T_l=\lambda(l+x-y-l_0)/l_0 \tag{2}$$

and

$$T_h=\lambda(h+y-h_0)/h_0 , \tag{3}$$

where λ stands for the elastic modulus of the string. When the system is in its equilibrium position, $x=y=0$ and $T_l=T_h$, so that (2) and (3) give

$$\lambda(l-l_0)/l_0=\lambda(h-h_0)/h_0 . \tag{4}$$

Let θ stand for the angular displacement of the pulley, I for its moment of inertia, and r for the radius of the groove. Then

$$\theta=y/r , \tag{5}$$

and since we are neglecting damping,

$$(T_l-T_h)r=I\ddot{\theta} , \tag{6}$$

From the five equations (2)-(6) it turns out to be possible to eliminate the five quantities T_l, T_h, l, h, and θ. We obtain

$$\ddot{y}+n^2y=r^2\lambda x/Il_0 , \tag{7}$$

where

$$n^2=\frac{r^2\lambda}{I}\left(\frac{1}{l_0}+\frac{1}{h_0}\right) . \tag{8}$$

Let the motion of the fork be given by

$$x=a\cos pt , \tag{9}$$

where $a>0$, and assume that the pulley rocks with a motion

$$y=b\cos pt . \tag{10}$$

On eliminating x and y from (7), (9), and (10), we find that b is determined by

$$b=\frac{r^2\lambda}{Il_0}\cdot\frac{a}{n^2-p^2}=\frac{h_0a}{h_0+l_0-p^2Ih_0l_0/r^2\lambda} . \tag{11}$$

Thus the phase of the pulley is the same as that of the fork or opposite to it according as h_0+l_0 is greater or less than $p^2Ih_0l_0/r^2\lambda$.

To find which part of the string experiences the greater change in tension, eliminate x, y, and a from (2), (3), (9), (10), and (11). We get

$$T_l=\frac{l-l_0}{l_0}\lambda+\frac{\lambda b}{h_0}\left(1-\frac{p^2Ih_0}{r^2\lambda}\right)\cos pt \tag{12}$$

and

$$T_h = \frac{h-h_0}{h_0}\lambda + \frac{\lambda b}{h_0}\cos pt\ . \tag{13}$$

From (12) and (13) we see that T_l has a greater range than T_h if

$$h_0 > 2r^2\lambda/p^2I\ , \tag{14}$$

and a smaller range if the inequality (14) is reversed.

On following out the method indicated above for determining the sense of rotation, we are led through a somewhat complicated series of special cases to this remarkably simple result: If (14) is satisfied, any rotation of the pulley is toward the fork; and if (14) is reversed, any rotation is away from the fork. This means that *if the end of the string is fastened, the sense of the rotation is independent of the length of the horizontal part of the string, the rotation is toward the fork when the vertical part of the string is sufficiently long, and the rotation is away from the fork when the vertical part of the string is sufficiently short.*

End of string loaded. Instead of having the end of the string fastened at W (Fig. 1), let it carry a load which has mass m and displacement z. Assume that the load has a simple harmonic motion of the same frequency as the fork. Since we are neglecting damping, the phase of the load must be either the same as that of the fork or opposite to that of the fork, and we may write

$$z = c\cos pt\ . \tag{15}$$

We obtain various equations which correspond to those that we used when the end of the string was fastened, but we find that we need an additional relation, and that this new relation may be obtained by regarding the load and the vertical part of the string as executing a forced vibration under the action of the pulley. After setting up this new relation, and then proceeding in a manner similar to that which we followed before, we finally obtain

$$b = a/\{1 + l_0[(h_0 - \lambda/mp^2)^{-1} - Ip^2/\lambda r^2]\}\ , \tag{16}$$

$$T_l = mg + \lambda b[(h_0 - \lambda/mp^2)^{-1} - Ip^2/\lambda r^2]\cos pt\ , \tag{17}$$

and

$$T_h = mg + \lambda b(h_0 - \lambda/mp^2)^{-1}\cos pt\ . \tag{18}$$

In this case we see that T_l has a greater range than T_h if $Ip^2/\lambda r^2 > 2/(h_0 - \lambda/mp^2)$, i. e., if h_0 lies outside of the region given by

$$\lambda/mp^2 < h_0 < (1 + 2mr^2/I)\lambda/mp^2\ ; \tag{19}$$

and that if h_0 lies inside of this region, it is T_h that has the greater range.

On carrying through the work to determine the sense of rotation we arrive again at a remarkably simple result: If h_0 lies inside of the region given by (19), any rotation of the pulley is away from the fork; whereas if h_0 lies outside of this region, the rotation is toward the fork. This means that *if the end of the string is loaded, the sense of rotation is independent of the length of the horizontal part of the string, and the rotation is toward the fork when the vertical part of the string is either sufficiently short or sufficiently long, and is away from the fork when the vertical part of the string has intermediate lengths.*

EXPERIMENT

Apparatus. In the present work I have used only one pulley, one string, and one frequency. The pulley is a brass one with cone bearings. Its radius is about 1.35 cm, and its moment of inertia about 19.0 g.cm^2. The string is the same braided fish cord that was used in previous work,[5,6] and has a linear density of about 2.24 mg/cm. The fork to which the string was attached is marked with a frequency of 100 double vibrations in a second, and was electrically driven by a second fork of the same frequency equipped with a mercury interrupter. When the amplitude of the fork was desired it was determined by reading in a micrometer microscope the width of a brightly illuminated line on the end of the prong to which the string was attached.

When transverse vibrations appear, it is sometimes possible to damp them out by holding one or two fingers lightly against the string. I have assumed that this procedure does not seriously affect the longitudinal vibration. There are however conditions under which the transverse vibrations are so strong that it is difficult to damp them out and feel sure that observations really represent what would happen if the vibration were purely longitudinal. Such cases are of course not included in my results.

General distribution of rotations. The theory indicates that the sense of rotation should be independent of the length of the horizontal part of the string. I have no observations which test this point. It is much easier to avoid transverse vibration in the horizontal part of the string when that part is short, and during a considerable part of the experimental work the length of the horizontal part of the string was between 4 cm and 5 cm.

When the end of the string is fastened, the theory indicates rotation toward the fork for the greater lengths of the vertical part of the string, and away from the fork for the smaller lengths. Experiment verified this prediction when the tension was 25 g, 30 g, or 35 g, but not when the tension was 5 g or 10 g.

When the end of the string is loaded, the theory indicates rotation away from the fork for intermediate lengths of the vertical part of the string, and toward the fork when the length is greater or smaller. Here again, observations with the smallest loads were either not consistent or not in agreement with the theory. But with loads of 20 g, 25 g, and 30 g, the various series of observations were pretty uniform in showing a rotation toward the fork for the greater lengths of the vertical part of the string, and away from it for the shorter. Rotation toward the fork for still shorter lengths was observed only twice, and neither of these observations is very reliable.

Elastic modulus of the string. If the end of the string is fastened, (14) shows that the rotation of the pulley reverses when

$$h_0 = 2r^2\lambda/p^2I \;; \tag{20}$$

and if the string carries a load, (19) shows that there is a reversal when

$$h_0 = (1+2mr^2/I)\lambda/mp^2 \;. \tag{21}$$

A fair approximation to the value of the h_0 in (20) or (21) can be obtained by adjusting the vertical part of the string until it has the shortest length for which rotation is toward the fork, and again until it has the greatest length for which rotation is away from the fork. The mean of these two may be taken as not far from h_0. (20) or (21) may then be used to calculate λ.

To determine λ directly, the string was hung from the ceiling, a point near the lower end was observed in a micrometer microscope, and a load on the bottom of the string was changed. It very soon became evident that the string took considerable time to adjust itself to a new load. In one case readings for the elongation after adding a load of 100 g were made for an hour, and at the end of that time the string was still stretching, and there was no indication that the stretching was nearly complete. Removal of all of the load except 10 g was followed by a similar slow recovery. The curves showing change of length against time were of the shape which is customary in cases of elastic after effect.

When there is an appreciable elastic after effect, values obtained for the elastic moduli depend on the time for which the changed load acts. I attempted to get values for the elastic modulus by alternately adding and removing a given load, and allowing several minutes after a change of load before taking any readings. This method did not lead to consistent results—perhaps partly because of irregular changes in the distance between the ceiling and the table on which the microscope rested.

The method finally adopted was to make a series of readings as rapidly as possible. A considerable aid in rapid reading was a camel's hair pencil which was mounted so as to rest lightly against the string just below the microscope, thus damping the swinging that was introduced when changing the load. A given increase was made in the load, the microscope read, the load decreased by an equal amount, the microscope read, the load again increased, and so on, until some forty or fifty readings had been made. This could be done in a little over half an hour, so that the elastic modulus was being determined for a force which varied at a rate a little slower than one cycle in a minute. Fig. 2 shows that the elastic modulus thus found for this braided cord is not independent of the tension—an effect which is probably to be explained by a straightening of the individual strands under the action of the heavier load.

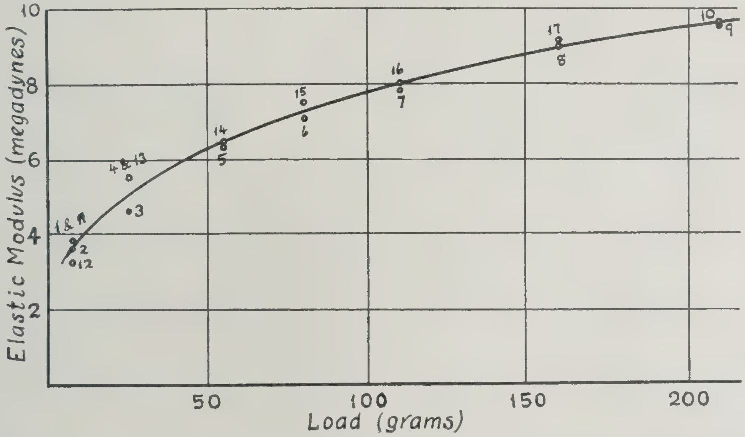

Fig. 2. Elastic modulus of the string as a function of the load. The numbers beside the plotted points give the order in which the values were obtained.

A comparison of theoretical and directly determined values of the elastic modulus is shown in Table I. The reversal of the rotation usually occurred with h_0 in the neighborhood of 25 cm. A third of the theoretical values in the table are the results of single determinations; the rest are means from two or three determinations. It will be seen that the theoretical values are at least of the right order of magnitude. For the smaller loads the agreement is probably as good as could be expected.

Whether the fact that the theoretical values are in most cases smaller than the observed has any significance is doubtful. In the cases of metals it is known[7] that the elastic moduli usually come out a little larger when determined dynamically than when determined statically. Wertheim[7] supposed that this difference was caused by the adiabatic heating and cooling in the dynamic experiments, and Kohlrausch[8] pointed out that any elastic after effect would also cause a difference in the same direction. In my results the difference is usually in the opposite direction, but it is very possible that when the theory has been extended so as to take account of the damping, the sign of the difference may be reversed. At any rate, the theoretical and the directly determined values agree much better than would have been supposed from the results on the general distribution of the positions for rotation in each sense.

TABLE I

Comparison between calculated and observed values for elastic modulus

Tension (grams)	End fastened Modulus (megadynes) calc.	obs.	Diff. %	End loaded Modulus (megadynes) calc.	obs.	Diff. %
15				41.5	43.0	−3.5
20				44.3	47.0	−5.7
25	48.4	50.7	−4.5	52.5	50.7	+3.6
30	43.8	54.0	−18.9	50.2	54.0	−7.0
35	49.5	56.7	−12.7	64.9	56.7	+14.5
40				50.6	59.2	−14.5

Friction between string and pulley. When the end of the string is loaded and there is no slipping of the string along the pulley, it will be seen from (16), (17), and (18) that if we know the elastic modulus of the string and observe the amplitude of the fork, we can calculate the tensions in both parts of the string. If we gradually increase the amplitude of the fork until slipping just begins—that is, until the pulley just begins to rotate—(17) and (18) give the limiting values of the tensions which we need in order to obtain from (1) a value for the coefficient of friction. A similar calculation can be made when the end of the string is fastened.

No observations were made for the purpose of determining the coefficient of friction. But in various cases the amplitude was increased by steps, and the rotation or lack of rotation was recorded for each amplitude. From these records there were selected for calculating the coefficient of friction twenty three cases in which it seemed likely that an observed amplitude was not much greater than that at which the pulley would just begin to rotate. In three cases (18) gave negative values for the smaller tension. In the remaining twenty cases the calculated coefficients were of the same order of magnitude as the observed. In every case the calculated value was, as we should expect, somewhat larger than the observed, but in only one case was it as much as ten times as large. On the average the calculated values were about five times the observed. When we consider the data from which these results were obtained, the agreement is perhaps as good as could be expected.

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[7] G. Wertheim, Pogg. Ann., Erg.-Bd. **2,** 1 (1848).
E. Warburg, Wied. Ann. **10,** 13 (1880).
Theodor Schröder, Wied. Ann. **28,** 369 (1886).
George A. Lindsay, Phys. Rev. **3,** 397 (1914).

[8] F. Kohlrausch, Pogg. Ann. **119,** 367 (1863).

CONCLUSION

On collecting the results of the three experimental tests of the theory for the rotation of the pulley we find: (1) That the general distribution of lengths of string for which the pulley actually rotated in a given sense tallies with the predictions of the theory only fairly; (2) that the values of the elastic modulus calculated from the lengths at which the rotation of the pulley reversed agree much better with the observed values; and (3) that the calculated values of the coefficient of friction between string and pulley, although very rough, probably agree with the observed values as well as could be expected.

I have pointed out that the sense in which the pulley rotates is not in all cases that which is predicted by the theory. In a considerable number of cases I have also found a reversal of rotation when the amplitude is sufficiently increased. In the present theory there is nothing to indicate any such reversal, and when comparing theoretical and experimental results I have aimed to use the rotation which occurred at the smaller amplitude.

When there are transverse vibrations of the string the theory will doubtless be more complicated. But before attempting to formulate that theory it would seem wise to see how the above theory is modified by taking into account the damping. It seems likely that the damping will modify the theory in such a way as to make the theoretical results agree more closely with those which are found experimentally. When this more extended theory has been developed and tested experimentally, it is entirely possible that the reversal of the sense of rotation of the pulley may provide a new means of studying the manner in which the elastic modulus of a cord or rope depends on the frequency with which the applied force changes.

SMITH COLLEGE,
November 24, 1925.

THE PHONIC WHEEL AND SURFACE TENSION OF LIQUIDS

By S. Ganapati Subramanyam

Abstract

A modification of Lord Rayleigh's stroboscopic method of measuring the velocity of ripples on the surface of liquids is described. A single, electro-magnetically driven tuning fork is used to generate the ripples and at the same time to drive by means of a Rayleigh synchronous motor a stroboscopic disk having as many slots as there are teeth on the motor armature. When the liquid surface is viewed through the disk the ripples appear stationary and their wave-length may be measured. A sample set of data is presented giving a value of 73.7 dynes/cm for the surface tension of water at 30°C.

LORD RAYLEIGH was the first to apply the measurement of the velocity of propagation of ripples to the determination of surface tension. He generated the ripples by the motion of a glass plate which was attached to the lower prong of an electrically driven tuning fork and dipped into the liquid. When ripples travel over the surface of a liquid, their velocity is so great that they cannot be observed by the unaided eye. If these ripples are viewed by intermittent light, the frequency of the flashes of illumination being the same as that of the source of ripples, then in each interval a ripple will travel over one wave-length and will occupy the position occupied by the preceding ripple at the commencement of the interval. The ripples appear stationary. To obtain such intermittent glimpses of the surface, the surface is usually observed through the prongs of a second tuning fork of the same frequency and maintained in vibration by the same circuit. Thus two tuning forks are found necessary for the success of the experiment. Moreover their periods must be exactly determined. Lord Rayleigh in his experiments on greasy surfaces[1] used a pair of forks. The frequency of the interrupter was about 42 per second so that the intermittent current could be used to excite a fork of frequency about 126. The beats between this and a standard Koenig fork of frequency 128 were counted at intervals and found to be sufficiently constant.

A method involving the use of only one fork is described here. Water is placed in a large porcelain developing dish. To one prong of a tuning fork a thin piece of aluminum plate is attached and the latter dips into the water. The fork is driven electro-magnetically and the intermittent electric current is made to drive a phonic wheel or Rayleigh synchronous motor. The phonic wheel consists of two electro-magnets and a rotating armature in the form of a soft iron wheel with 30 teeth. It was fitted with a permanent friction-wheel and was used with a stroboscopic disc having 30 slots. A timing attachment was arranged to ring a bell at every 100 revolutions of the motor spindle. The phonic wheel is made to run with its axis vertical. The porcelain dish is so placed underneath the stroboscopic disc that the surface of water in it is capable of being viewed through the slots in the disc. Thus the single fork acts the part of an interrupter as well as an exciter of ripples. An incandescent bulb was suspended about a metre and half above the surface of water, whose ripples then cast a series of shadows on the bottom of the white porcelain dish. Dividers are arranged also to cast a shadow and they are so adjusted that the two ends of the dividers' shadow coincide with the corresponding parts of the first and last number of waves that can be easily counted.

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[1] Rayleigh, Scientific Papers, Vol. III, p. 387.

To start the motor it is speeded up by hand and then by proper manipulation kept rotating at approximately this speed until the position of the wheel becomes right and the motor falls in step with the interrupted currents from the fork. As the armature rotates, the magnetic circuit of the electromagnet is approximately closed whenever a pair of teeth are opposite the pole pieces. As there are 30 teeth in the armature, the circuit is closed 30 times during every revolution. The interval between any two closures of consecutive teeth is also the interval between the appearance in the field of view of any two consecutive slots in the disc and thus the ripples are seen by intermittent illumination, the frequency of the flashes of illumination being the same as that of the fork which excites the ripples.

The following is a sample set of observations on water at 30C. The mean time for 300 revolutions was 181.6 sec. Since there were 30 slots on the disk the time interval between flashes was .02016 sec. This as noted above is also the period, τ, of the fork, The dividers were set with their points 5 cm apart and there appeared between them 8.4 wavelets as viewed stroboscopically. This gave for the wave-length, λ, a value of 0.595 cm. The surface tension of the water may then be calculated by Rayleigh's formula

$$T=\frac{\lambda}{2\pi\tau}-\frac{g\lambda^2}{4\pi^2}$$

The value obtained is 73.7 dynes/cm.

Arts College,
Rajamundry, S. India,
November 19, 1925.

BOOK REVIEWS

The Fundamental Concepts of Physics in the Light of Modern Discovery. Paul R. Heyl.—This little book is a wholly admirable summary of the evolution of the leading physical theories of the present day. In simple language, within the comprehension of any educated reader, and with frequent enlivening touches of poetry and humor, it traces the development of the concepts of matter, heat, electricity and energy through the eighteenth and nineteenth centuries down to the startling advances of the past quarter-century. The foreword contains an eloquent appeal for a greater breadth of vision on the part of the scientific worker. "We physical scientists feel this most keenly, for modern thought presents to us concepts of a strange and bewildering nature, generalizations so broad as to strain our vision to include them in their entirety. We are gasping like our ancestor, the lung fish, in a dry season. And yet there are minds which have produced these concepts and laid out these generalizations; and there are many more who, while they cannot produce, are able to follow. The rest of us are confronted with the stern alternatives of keeping up with the procession or falling out."

In Chapter I we find an account of the development and decline of the caloric and phlogiston theories. The essentially materialistic character of the science of the period, combined with appeal to the supernatural when material explanations failed, is emphasized. Various respects in which the thought of the eighteenth century anticipated our modern theories are pointed out, for example the transformation of matter into radiation, the two-fluid theory of electricity, and potential energy. The second chapter recounts some of the chief discoveries of the nineteenth century. Among the achievements of this century are discussed especially the growth of the concept of energy and the correlation of the scattered ideas of the century preceding. Excellent perspective views are given of Mayer's first determination of the mechanical equivalent, and of the principle of the conservation of energy. Unusually clear expositions of the second law of thermodynamics and its limitations, and of entropy, are given, ending with the following bit of wisdom: "Nothing, to the popular mind, can be less akin than poetry and mathematics; and the concept to which we refer, that of entropy, is abstract and mathematical to a high degree, being defined by an integral, and not capable of being as readily visualized as its sister concept of energy. Nevertheless there may be such a thing as poetry under an integral sign, incongruous as the association may appear." Comparatively little space is devoted to Maxwell's great contributions. The final chapter, on the twentieth century, or the "Century of Hope," occupies nearly half of the book. The author constantly points out the evolution of present ideas from those of the past, as well as the need of further advancement into the unknown. The outstanding features of this chapter are the accounts of the modern theory of matter, including the quantum theory, and relativity. With great clarity Einstein's deductions of the correlation of gravity and inertia, and of the relation between matter and energy, are described, and the difficulties in the way of experimental verification are noted. These pages on relativity and its shortcomings contain the best popular exposition of the subject that we have yet seen. Unfortunately the book was written just too early for a consideration of Miller's latest experiments on ether drift.

A good list of references to original memoirs is provided. Nevertheless one cannot help wishing that the author had been more explicit as regards dates of discoveries and the names of those to whom some of the advances are due. As to errors, it is perhaps unfair to expect rigorous exactness in a book for popular reading, yet the statement on page 73, that the quantum concept "atomizes energy into indivisible units, not all of the same size, but integral multiples of the smallest of them," without mention of the effect of frequency, seems needlessly misleading, likewise the statement on page 83, that "the magnetic attraction can be cut off by a suitable screen." The book concludes with a consideration of the attitude of the scientist toward the future. The following quotation is typical of the picturesque style of the book: "The physicist, above all others, remembers how Galileo invited the learned men of his day to look through his telescope and how they refused to do so; but he also remembers how the Pilgrim made his progress through Vanity Fair, urged ceaselessly on all sides to buy this, that or the other brilliant trinket, and how he held steadfastly to his way, clutching to his bosom that which had proved itself to be his only safe guide through all the perils of the way he had come." Pp. xii+112. Williams & Wilkins Company, Baltimore, 1926. Price $2.00.

WALTER G. CADY

A Textbook of Physics. (Third edition). L. B. SPINNEY.—The former editions of this book have won for themselves a place among the best American college texts on physics, and this high level promises to be maintained by the third edition. The book is distinguished by its clarity of statement, excellent figures, and well selected numerical examples. While the latter are for the most part the same as in the second edition, still in many cases numerical values have been altered and some new examples have been added. Inasmuch as some acquaintance with trigonometry is assumed, trigonometrical expressions might well have been introduced more freely, especially in the resolution of forces in the chapters on statics and on magnetism. The judicious emphasis placed upon the more essential facts and principles is an excellent feature; but the revision of some of the chapters, particularly with respect to such topics as radio telegraphy and modern atomic theory, could have been more thorough. While realizing that this is a matter of opinion, the reviewer cannot refrain from pointing out certain matters that have been either omitted or rather scantily treated. These are, for example, shear and rigidity; self and mutual inductance, and the transformer; the ear; fluorescence and phosphorescence; the Foucault pendulum; photo-electricity and quanta. Thermoelectricity is hardly mentioned. Excellent historical notes are given here and there, but the name of Röntgen appears only in the index, and there is no mention, in the paragraphs on atomic structure, of the chief names concerned with its modern development. On pages 443, 444 we read that the proton "has always the same mass," and that protons and electrons "appear to be equal in diameter." As in too many textbooks, the correct explanation of the part played by the dielectric in the phenomenon of residual charge and in the experiment with the "dissectable jar" is not given. As we have stated, these criticisms are largely a matter of opinion. In the main, Professor Spinney has covered the field with a degree of care and completeness that makes the book distinctly to be recommended.—Pp. xiii+635, 420 figs. The Macmillan Company, New York, 1925.

WALTER G. CADY

Die Neuere Entwicklung der Quantentheorie. Second Edition.—A. LANDÉ (Wissenschaftliche Forschungsberichte, Band V)—The new edition of this book indeed merits the statement that it is "fully revised", for it is twice the length of the first edition (which carried the somewhat different title "Fortschritte der Quantentheorie"). A large number of diverse subjects are summarized, including multiplet structures and the anomalous Zeeman effect, specific heats, the mechanics of the hydrogen atom, and the quantization of perturbed systems by Bohr's method of variation of constants. Einstein's recent work on the degradation of gases is very properly presented in greater detail than many of the other more familiar subjects. In discussing chemical constants and spectroscopic magneton numbers, the author glosses over apparent experimental contradictions, probably because the book does not in general include extensive comparisons with experiment. The first chapter, which is entirely new, is devoted to the structure of radiation.

Here both corpuscular light-quants and virtual oscillators are presented as helpful concepts.

The book does not purport to be a complete text, but instead, to quote the author, is intended for "readers who are content with a brief recapitulation of the elements of the quantum theory." The aims of a good syllabus are fulfilled, for the subject matter is usually well chosen and accurately presented. The style is of necessity a condensed one, and this may make certain chapters rather difficult for readers not already familiar with the quantum theory.

An index is included, and also a bibliography in which over 300 papers are listed. Consequently the book is well worth having for reference purposes. The bibliography is fairly complete in its listing of German papers, but certainly the opposite for those in English. References, for instance, are given to the work of Fues, Schrödinger, van Urk, and Wentzel on atomic force fields, but there is no mention of the contributions of Hartree and Lindsay. Several other omissions of like nature could also be cited. The correlation of text and bibliography is poor. Important contributions mentioned in the text are not listed at all in the bibliography (as, for instance, the recent work of Compton and Simon on scattered light-quants), while the bibliography contains numerous papers without any very obvious relation to the text-material, though this is obscured by the unfortunate omission of the titles of papers. The bibliography on the correspondence principle, for instance, contains a miscellaneous, incomplete assortment of papers on the polarization of resonance radiation. The theory of specific heats is presented in the text after the early Ehrenfest method, but bibliography references are given to the more satisfactory Reiche theory with, of course, no mention of American contributions.

One must indeed admire the celerity with which the book has been printed, for it is ready for distribution only two months later than the date of writing. Consequently, the references to the German papers are up-to-the-minute, including even a section on matrix dynamics. In view of the obvious speed of writing, one can perhaps excuse the occasional misspelled names in the bibliography.—Pp. xi+180, 14 fig, Steinkopff, 1926. 12 marks; bound, 13.20.

J. H. Van Vleck

PROCEEDINGS
OF THE
AMERICAN PHYSICAL SOCIETY

Minutes of the Stanford Meeting, March 6, 1926.

The 138th meeting of the American Physical Society was held at Stanford University on March 6, 1926. Professor Fernando Sanford presided. Morning and afternoon sessions were held with an attendance of about eighty. The Society held an informal luncheon at the Stanford Union, attended by fifty-five members and guests.

The regular scientific session consisted of 27 papers, (one of which was read by title) abstracts of which are given on the following pages. An **Author Index** will be found at the end.

DAVID L. WEBSTER,
Local Secretary for the Pacific Coast.

ABSTRACTS OF PAPERS

1. The Compton effect and virtual oscillators. P. A. Ross, Stanford University.—In recent papers by Slater and by Bohr, Kramers, and Slater an attempt has been made to reconcile quantum theory and wave theory by postulating certain "virtual oscillators" which shall be capable of absorbing waves to synthesize quanta. If such virtual oscillators were in a region illuminated by monochromatic radiation from two sources of the same frequency it would seem reasonable that the oscillator should build up its quanta by absorbing radiation from both sources and thus acquire momentum along the resultant Poynting vector. If this absorbed quantum were passed over to an electron to be scattered according to the Compton equation, the angle of scattering and consequent change of wave-length should correspond, not to the angle between the scattered beam and either incident radiation, but to the angle between the scattered beam and the resultant Poynting vector. This was tested by placing a graphite scattering block between two x-ray tubes driven in parallel from the same transformer. Two spectrographs were set up. One received radiation scattered at 90° to both incident beams. The other received radiation at angles of 125° and 55°, respectively, from the two beams. The normal Compton effect was observed. The above theory would demand no shift.

2. The Doppler principle and the quantum hypothesis. G. E. M. JAUNCEY, Washington University.—The relativity theory demands that when an atom at rest changes from an energy state W_1 to an energy state W_2 there is a change of mass from M_1 to M_2. Hence emission of radiation is accompanied by loss of mass. Suppose an atom of mass M_1 moving with velocity $\beta_1 c$ emits a quantum in the forward direction, after which the atom has a mass M_2 and velocity $\beta_2 c$. Conservation of energy requires $M_1 c^2/\sqrt{1-\beta_1^2}=h\nu+M_2 c^2/\sqrt{1-\beta_2^2}$, while conservation of momentum requires $M_1\beta_1 c/\sqrt{1-\beta_1^2}=h\nu/c+M_2\beta_2 c/\sqrt{1-\beta_2^2}$. Eliminating β_2 and solving for ν, we obtain ν as a function of β_1. Now calling ν_0 the value of ν when $\beta_1=0$, we obtain $\nu/\nu_0=(1+\beta_1)/\sqrt{1-\beta_1^2}$. If β_1 is small and we put $\beta_1 c=v$, then $\nu/\nu_0=(c+v)/c$. The formula for the Doppler principle has thus been obtained without the use of the classical wave-theory.

3. The continuity of the x-ray spectrum at a wave-length twice the short-wave limit. D. L. Webster, Stanford University.—Planck's theory of heat radiation indicated a probability that an oscillator might emit any integral number of quanta at once, the probability of a number greater than one being greatest under conditions giving most rapid absorption. Since the absorption of energy from a cathode ray is presumably very rapid, one might expect double-quantum emission in x-rays. Evidence for this would appear in the continuous spectrum as a discontinuity of slope at twice the short-wave limit. Discontinuities of this sort in observed spectra have been interpreted as second-orders of the short-wave limit, and Kirkpatrick verified this interpretation, approximately, by absorption tests. The need for such means of eliminating second orders practically vanishes with the use of diamond, in which Bragg found the second order very faint. In work on the use of diamond for spectral intensity measurements, the author has tested the continuity of spectra and isochromats of tungsten, finding no evidence of any double-quantum radiation. The change of slope of an isochromat at twice the excitation voltage, if it exists at all, is not over a very few percent of that at the excitation voltage itself.

4. The crystal structure of $[N(CH_3)_4]_2 PtCl_6$. Maurice L. Huggins, Stanford University.—Using Laue and spectrum photographs and the theory of space groups, the structure of tetramethyl-ammonium chloroplatinate has been determined. The structure has cubic symmetry, with $a_0=12.65$A. Pt and N atoms are disposed as are the Ca and F atoms in CaF_2 (special cases $4b$ and $8e$ in Wyckoff's "The Analytical Expression of the Results of the Theory of Space-Groups"). Each Pt is surrounded by 6 Cl atoms ($24a$) at corners of a regular octahedron, and each N is surrounded by four C atoms ($32a$) at corners of a regular tetrahedron. The symmetry is that of the space-group $O_h^5(Oi-5)$ or that of $O^3(O-3)$. Assuming the N–C distance to be 1.47A, the best agreement with the data is obtained when Pt–Cl is taken as about 2.35A. This research was done while the author was National Research Fellow in Chemistry at the California Institute of Technology.

5. The crystal structures of anatase and rutile, the tetragonal forms of TiO_2. Maurice L. Huggins, Stanford University.—Using Laue and spectrum photographs and the theory of space-groups, the structure obtained by Vegard for anatase and that obtained by Vegard and by Greenwood for rutile have been verified. The unit cell of anatase has the dimensions $a_0=3.78$A and $c_0=9.50$A; it contains Ti atoms at (000) $(0,\frac{1}{2},\frac{1}{4})(\frac{1}{2},0,\frac{3}{4})(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and O atoms at $(00u)(0,\frac{1}{2},u+\frac{1}{4})(\frac{1}{2},0,u+\frac{3}{4})(\frac{1}{2},\frac{1}{2},u+\frac{1}{2})(00\bar{u})(0,\frac{1}{2},\frac{1}{4}-u)$ $(\frac{1}{2},0,\frac{3}{4}-u)(\frac{1}{2},\frac{1}{2},\frac{1}{2}-u)$ where $u=.20\pm.01$. The symmetry of this arrangement is that of the space group $D_{4h}^{19}(4Di-19)$. For rutile $a_0=4.58$A and $c_0=2.95$A; Ti atoms are in the positions $(000)(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and O in $(uuo)(\overline{uu}o)(\frac{1}{2}-u,u+\frac{1}{2},\frac{1}{2})(u+\frac{1}{2},\frac{1}{2}-u,\frac{1}{2})$, where $u=.30 \pm.01$. The symmetry is that of $D_{4h}^{14}(4\ Di-14)$. This research was done while the author was National Research Fellow in Chemistry at the California Institute of Technology.

6. PP′ groups in the elements S(I) to K(IV). J. J. Hopfield and G. H. Dieke, University of California.—Two new *PP′* multiplets representing double electronic transitions in A (III) and K (IV) have been added to those already observed (Hopfield, Phys. Rev. **23**, 766 and **26**, 282). The final state of these four groups is the lowest *P* level, which is also the valence level. The six lines of these multiplets are clearly resolved on our spectrograms of S, Cl and A. The position of the multiplet in K(IV) was predicted and then found among Millikan and Bowen's data. The wave numbers of the multiplets are: S(I), 72380, 72174, 72019, 71985, 71805, 71625; Cl (II), 93995, 93626, 93357, 93305, 92995, 92669; A(III), 114797, 114216, 113803, 113687, 113228, 112690; K (IV), 135691, 134745, 134174, 133326, 132222. Bowen and Millikan (Phys. Rev. **26**, 150) have also observed *PP′* groups in a series of elements. A comparison of this work with their's shows (1) that the structures of the groups are alike except that in the present case the triple levels are inverted, (2) that the successive frequency differences of the groups S (I) to K (IV) are nearly equal to those of Mg (I) to Cl (VI), (3) that the difference in frequency between the S (I) and the S (V) multiplets is approximately equal to the separation of the Cl (II) and the Cl (VI) groups. This multiplet has not been found in O (I).

7. Series due to halogens in infra-red absorption spectra of organic compounds. Joseph W. Ellis, University of California, Southern Branch.—Absorption band series, attributed to carbon-hydrogen and carbon-carbon bonds have previously been reported by the writer. The absorption spectra of methylene chloride and chloroform contain, in addition to the C-H series, bands which fit a linear, or "harmonic," series whose initial wave-length member seems to be 16.8μ. The remaining bands of the short wave-length spectra can readily be accounted for by combinations between this series and the C-H series. Similarly, bands in the spectra of methylene bromide and bromoform, and methyl iodide and methylene iodide, can be grouped into linear series, which start at 17.2μ and 17.5μ, respectively. Members of combination series can also be identified in these latter spectra. Members of these series can also be found in spectra of more complicated molecules containing halogen atoms, but the spectra are complicated by the presence of bands due to C-C pairs. That these bands are due to the presence of halogen atoms seems certain; that the presence of hydrogen in the molecule is necessary for their appearance seems also certain, as carbon tetrachloride and tetrachlorethylene, containing only carbon and chlorine atoms, show no absorption in the short wave infra-red region.

8. On the specific heat of hydrogen. G. H. Dieke, University of California.—A recalculation of the specific heat of hydrogen has been made on the basis of the new development in band spectra. The *probabilities a priori* have to be of the form $p_j=j+a$, where a can be left undetermined. (j is the total moment of momentum of the molecule.) The results are: (a) m (rotational quantum number) $=\frac{1}{2}, 1\frac{1}{2}, 2\frac{1}{2}, \ldots$ Only moderate agreement between theory and observations for any choice of the p_j; (b) $m=1\frac{1}{2}, 2\frac{1}{2}, 3\frac{1}{2}, \ldots$ (suggested by the visible H_2 bands (Fulcher bands). (Dieke, Proc. Amsterdam, **27**, 490. See also Hutchisson and Van Vleck, Phys. Rev. **25**, 243) gives much better results with the p_j to be expected by theory; (c) $m=j\pm\frac{1}{4}$, which is suggested by the alternating intensities in the Fulcher bands gives also good agreement for low temperatures. Other assumptions, less probable, also give curves which agree fairly well at low temperatures. The present measurements are not sufficient to decide in favor of one particular hypothesis. For higher temperatures the non-rigidity of the molecule would change the curves considerably. There are, however, no data as yet which would allow with any certainty the calculation of the curves for a non-rigid molecule.

9. New oxygen bands between λ2000–2300. Vivian M. Ellsworth and J. J. Hopfield, University of California.—Sixteen new bands due to ionized oxygen have been photographed in the region 2000–2300. They occur in pairs degraded to the red. The pairs have a constant frequency difference of 200 units. The bands appear to be an extension to the ultra–violet of the group of electronic O_2^+ bands arranged in Deslandres progressions by Johnson. Mecke and Birge made quantum assignments of the group. The progression having the lowest final state according to Mecke's interpretation, is now extended by two members having higher initial states than those previously reported. The total number of initial states now indicated is ten. A new progression having a still lower final state appears and fits the scheme. This necessitates raising the previously assigned quantum numbers for the final states by at least one unit. Other bands which are too dim to measure but which have the characteristic appearance of the group and may belong to it, appear farther to the ultraviolet. The 0,0 band and those in its neighborhood are still missing and the general character of the schematic arrangement is unchanged by the additions.

10. On the absorption bands of nitric oxide. H. SPONER and J. J. HOPFIELD, University of California.—It was recently shown by one of us that the final state of the third positive group of nitrogen (γ bands) is the stable state of NO. Now it was found from absorption plates in NO taken by Dr. Leifson and kindly sent to us, that also the β bands occur on these plates proving that the β and the third group bands have a common final state as was suggested by Mulliken and by Birge. This progression from the normal state extends the scheme of the β bands from $n''=3$ (final) to $n''=0$ ($n'=2$ to 5 initial). According to a suggestion by Mulliken, the stable state is a double p level corresponding to aluminum, while the initial state of the third positive group bands corresponds to an s level and that of the β bands to a double d level.

11. The fine structure of the λ4842 band of AlO. WILLIAM C. POMEROY, University of California.—The rotational energy of the AlO molecule has been represented by $F=Bm^2+Dm^4+Fm^6+Hm^8$ where $m=k-\epsilon$. k is a half integer representing the resultant molecular momentum. Approximate values of ϵ are .0074 and .01 for the initial and final states respectively. Vibrational frequencies for infinitesimal vibration calculated from Kratzer's formula, $\omega=\sqrt{-4B^3/D}$, agree with values obtained from vibration data alone within 0.2%. The doublet separation of band lines was represented as a function of k of the initial state for both the P and R branches by a single equation, $\Delta\nu=.0116k+12\times10^{-6}k^2-7\times10^{-11}k^4$. Attributing the doublets to a double energy level in the initial state $(F')^{+-}=(.6019\pm6\times10^{-6})m^2-(1.1630\times10^{-6}\pm3.5\times10^{-11})m^4+.54\times10^{-12}m^6$ where $m=k-0.0074\pm0.00482$; $(F'')=.6386m^2-1.1094\times10^{-6}m^4-.43\times10^{-12}m^6-5.2\times10^{-18}m^8$. Throughout the measured range ($k=140.5$), observed frequencies of lines of the (0,0) band agree with those calculated from $P_k^{+-}=20635.27+(F'_{k-1})^{+-}-F_k''$; $R_k^{+-}=20635.27+(F'_{k-1})^{+-}-F_k''$ with residuals rarely exceeding .04 cm^{-1} (.01A).

12. Theory of intensity distribution in band systems. EDWARD CONDON, University of California.—Franck (Trans. Faraday Soc. 1925) has given a simple mechanical explanation for the large change in vibration quantum number in the absorption bands of cold (non-vibrating) iodine molecules. It is assumed that the electron transition affects only the binding of the atoms, leaving unaltered the relative nuclear separation. Quantitative treatment of this model by the author embodies the application to transitions where the molecule is vibrating in the initial state and assumes further that the nuclear velocities are not changed by the electron transition, explaining thereby the major aspects of the observed intensity distributions in band systems in emission and absorption. The theoretical expression is: $n''=\pi\omega''md^2/h+\frac{1}{2}(\omega'/\omega''+\omega''/\omega')n'-\sqrt{n'}\sqrt{4\omega''/\omega'(\pi\omega''md^2/h)}\sin\theta+\frac{1}{2}(\omega'/\omega''-\omega''/\omega')n'\cos 2\theta$. Here n'' and n' are the final and initial vibration quantum numbers, ω'' and ω' the final and initial vibration frequencies, m the reduced mass, d the difference in equilibrium separation in the two electronic states and θ the phase of the vibration at the instant of electron transition. Applied to the meager experimental data for emission bands of AlO, CO, CO$^+$, N_2 (2nd pos. group), N_2^+ (1st neg. group), SiN and I_2 the theory is in good accord with the facts.

13. The heat of dissociation of non-polar molecules, as determined from band spectra, and from other sources. RAYMOND T. BIRGE and HERTHA SPONER, University of California.—The limiting amount of vibrational energy which a diatomic molecule can possess is given by $E_n=h\int_0^{n_o}\omega^n dn$, where ω^n is the frequency of vibration, as a function of the vibrational quantum number n, and n_o is the value of n for $\omega^n=0$. For *non-polar* molecules n_o is finite, for polar molecules it is infinite. Usually the $\omega^n:n$ curve for the stable molecular state is strictly linear, over the known range, and its linear extrapolation to $\omega^n=0$, *for essentially non-polar molecules*, seems to give the true value of E_n to within half a volt. Since the molecule dissociates into two stable atoms, $E_n=Q$, the heat of dissociation. When the molecule dissociates, while excited by E_e units of electronic energy, the products of dissociation seem from previous work on iodine to be one stable and one excited atom (of excitation energy A). Hence $Q+A=E_e+E_n$. For dissociation from certain excited states of O_2, CO, and NO, A seems to be negligible (see following abstracts). Values of Q have thus been obtained for O_2, O_2^+, N_2, N_2^+, CO, CO^+, and NO. These values are self-consistent and are also consistent with data from other sources.

14. The heat of dissociation of O_2 and O_2^+. Raymond T. Birge, University of California.—Using new data by Hopfield and Leifson, the $\omega^n{:}n$ curve for the excited state of the Schumann bands of oxygen is known almost to $\omega^n=0$. The true value of E_n (see preceding abstract) is thus known to ±0.01 volt. $E_e+E_n(=Q+A)=7.05$ volts, and A is probably only 0.01 or 0.03 volts. (The stable state of oxygen atom is a triple p level, of 0.01 and 0.02 volts spacing.) Hence the true heat of dissociation of O_2 is 7.05 ± 0.03 volts. Mulliken finds that the Runge bands are a portion of the above system, and the new data thus available for the stable state of O_2 yield an apparently linear $\omega^n{:}n$ curve from $n=0$ to 17. Its linear extrapolation (to $n_o=69$) gives $E_n=Q=6.66$ volts, showing the probable error (±0.5 volts) of such an extrapolation. The O_2^+ bands give $Q'=6.46$ volts, from a linear $\omega^n{:}n$ curve for the stable state, and 6.49 volts from a linear excited state curve, (O_2^++Q' volts$=O+O^+$). I' (ionization potential of atom) $=13.54$ volts. Therefore I (ionization potential of molecule) $=14.1$ volts, since from conservation of energy, $I+Q'=Q+I'$, always. These values agree with the Hogness and Lunn results of positive ray analysis of oxygen.

15. The heat of dissociation of N_2 and N_2^+. Hertha Sponer, University of California.—Q for N_2 has been suggested by the writer as about 11.4 volts, from the energy of active nitrogen. The ω^n data for the stable state are unknown. The $\omega^n{:}n$ curve for the final state of the first positive group gives $E_e+E_n=8.0+3.87=11.87$ volts. Because of the non-linear character of the curve, this result is only approximate. The above value is supported by the results of Hogness and Lunn, who get N^+ ions at 24 volts has the result of a collision of an excited N_2 with a neutral molecule. The explanation can be given by the process $N_2^{exc}\,(24)\rightarrow N+N^+(13\text{–}14)+Q(11.4)$. The value for ionization of $N(=13\text{–}14)$ is estimated roughly from spectroscopic data. For N_2^+ one obtains 9.06 volts for Q' from a linear graph for the final state, and 9.7 volts from the linear extrapolation of an actual negatively curved $\omega^n{:}n$ graph. Hence this last result should be too large. Using the $I+Q'=Q+I'$ equation with the known $I=16.5$ volts, $16.5+9.06=11.4+I'$. This gives $I'=14.16$ volts, to be compared with the above 13–14 volts. The agreement is within the limits of error.

16. The heat of dissociation of CO, CO^+, and NO. Raymond T. Birge and Hertha Sponer, University of California.—A strictly linear $\omega^n{:}n$ curve for the stable state of CO (known to $n=22$) gives $Q=11.18$ volts. The next higher electronic level gives $Q=12$ volts, but is more uncertain. The third level is unsuitable for this work. The heat of sublimation of diamond (6.11 volts) and other known chemical data, combined with the now known value $Q=7.05$ volts for O_2, give $Q=10.78$ volts for CO, a probably better value than 11.18. Only the stable state of CO^+ gives a linear $\omega^n{:}n$ curve and the resulting $Q'=9.82$ volts, (CO^++Q' volts$=C+O^+$ assumed). The known I for CO is 14.2 volts, and I' (of oxygen atom) is 13.5 volts. Hence $I+Q'=Q+I'$ becomes $14.2+9.82=10.78+13.5$, a satisfactory agreement. For NO only the excited state of the gamma bands gives a linear $\omega^n{:}n$ curve. The resulting $E_e+E_n=17.19$ volts. Assuming $Q=7.05$ for O_2 and 11.4 for N_2, and knowing $N_2+O_2+1.9$ volts$=2$ NO, $Q=8.27$ volts for NO. Since $E_e+E_n=Q+A$, A equals 8.92 volts, and this type of dissociation of NO seemingly results in a neutral nitrogen and an 8.9 volt excited oxygen atom, agreeing with the known resonance potential of oxygen (9.1 volts).

17. Rate of neutralization of the field in the Braun tube with external electrodes. A. M. Cravath and L. T. Jones, University of California.—This is a study of a problem which arose in the investigations of Jones and Tasker, J.O.S.A., **9**, 471, 1924. The field of the external electrodes is rapidly neutralized by the collection of ions and electrons on the tube walls, so that the deflection is not proportional simply to the applied voltage. The neutralization proceeds like the discharge of a condenser with time constant $RC=\tau$. This time constant τ, which is a reciprocal measure of the rate of neutralization, was calculated from current measurements made with internal electrodes, and was measured directly by photographing the variation of deflection with time, the two values for the tube used being 0.002 and 0.0013 seconds. From the latter value it is calculated that for sinusoidal voltages of 60 and 7000 cycles per second the deflection should lead the applied voltage by 65° and 1° and the amplitudes should be reduced to 40% and 99.98% of the values they would have in the absence of neutralization.

18. **Phase and magnitude of deflections of Braun tube beam with internal and external electrodes.** R. A. Jack and L. T. Jones, University of California.—Photographs showing a 90° phase difference between the deflections of a cathode beam of a Braun tube with 60 cycle alternating potential applied to external and internal electrodes, respectively, were published by Jones and Tasker. (J.O.S.A. **9**, 471, 1924; Phys. Rev. **23**, 777, 1924). The following work has been done to determine the phase difference at different frequencies and to determine the deflection as a function of frequency with external electrodes. At the lower frequencies the deflection is a function of the frequency, while at the higher range the deflection becomes constant. At high frequencies the deflections with external and internal electrodes are apparently equal. By the use of Lissajous' figures, with the internal and external sets of electrodes at right angles, the phase difference has been found to disappear at high frequencies. Work is being continued to complete the frequency range from 60 to several million cycles.

19. **The ionization of oxygen as interpreted by positive ray analysis.** T. R. Hogness and E. G. Lunn, University of California.—Positive-ray analysis of the products of electron-impact ionization in oxygen shows that the percentage of the ions, O_1^+ and O_2^+ is independent of the pressure of oxygen. Evidence is thus given that O_1^+ and O_2^+ are formed by independent processes, and hence that an impact electron can dissociate oxygen with the formation of the atomic ion. The ionization potentials for the formation of O_2^+ and O_1^+ were found to be 13 and 20 volts, respectively. The latter, together with Hopfield's series limit, gives 6.5 volts (150,000 calories) for the heat of dissociation of oxygen.

20. **Mobilities of gas ions in HCl.** Leonard B. Loeb, University of California.—Mobility measurements were made in pure dry HCl gas using the Franck modification of the Rutherford method with an alternating potential of square wave form. The average mobility for the positive ion at 20°C and 760 mm was found to be 0.65 cm/sec per volt/cm and 0.56 cm/sec per volt/cm for the negative ion. This measurement of a negative mobility definitely less than a positive mobility constitutes the first exception to a general rule previously assumed from observation which indicated that the negative ion had a mobility either equal to or greater than the positive ion, *but not less*. The inverse pressure law of mobilities was found to hold for both positive and negative ions down to 16.3 mm pressure. It was concluded from this that the constant of attachment of electrons to HCl molecules to form negative ions was nearly as low as that for Cl_2 gas. Finally, measurements of mobilities in mixtures of air and HCl showed unmistakable signs of a cluster ion formation in this gas, the mobilities being lowered by marked amounts for fractions of a percent of HCl gas.

21. **On the theory of electrolytes.** F. Zwicky, California Institute of Technology.—The theory of Arrhenius accounted for the different properties of electrolytic solutions with the hypothesis of complete or partial dissociation of the molecules of the solute, the degree of dissociation being a function of the concentration. After it had been shown,

that for strong electrolytes the dissociation is complete at all concentrations, another explanation for the behavior of such solutions had to be found. Concerning the osmotic equation of state and the electrical conductivity, the problem was solved by Milner and Debye in introducing the so-called "ion-atmospheres." The ordinary equation of state (thermal and caloric), however, has not yet been treated and it is now proposed to deduce it in a general way. It appears that the effects due to the electric charges of the ions are predominant. These effects are, in outline, the following: (1) formation of ion-atmospheres; (2) electric polarization of the solvent; (3) attraction of the molecules of the solvent towards the ions with resulting high pressures (as great as 50000 atm.) in the vicinity of the ions. The mathematical treatment of these effects gives results, which are in complete agreement with the observed data of specific heat, compressibility, thermal coefficient of expansion and volume-contraction on solution.

22. **Variations in Hall effect and thermoelectric power due to changes in crystallinity.** L. J. NEUMAN, University of California.—Variations of the Hall constant due to changes in crystallinity have been investigated. Strain-hardening was found to produce an increase in R for Bi from -5.78 to -9.27. In Sn and Cu, however, the value of R is decreased by similar treatment. Thermoelectric effects between specimens of Fe, All Ni, Zn, Cu, Au, and german silver possessing different degrees of crystallinity have been measured for temperatures from 0°C to 1000°C. Thermoelectric powers of over 2 microvolts per degree C have been observed between annealed and strain-hardened specimens of a single metal. The sign of the e.m.f. is the same for all of the metals investigated. Thermoelectric effects between single capillary crystals are discussed and data given.

23. **Errors in measurement of the Thomson effect and an anomalous effect in Bismuth.** MARCUS O'DAY, University of California.—Especial care must be taken in the measurement of the Thomson Effect that there is no chance for leakage of the main current to the measuring apparatus. Experiments conducted by the writer have shown that with ordinary precautions against leaks, a small stray current to the measuring apparatus would behave just as a normal Thomson Effect if thermocouples are used for the measurement of temperature. Using extreme precautions against this and isolating the thermocouples in pyrex glass tubes the writer has worked on the effect in bismuth using heavy currents. Several thermocouples were placed along the bar and the change of temperature measured upon reversal of the main current. However, instead of the change of temperature being proportional to the temperature gradient, the writer finds a direct proportionality to the temperature. It is suggested that this may be due perhaps to an asymmetrical thermal conductivity due to the method by which the bars were cast. It was found upon examination of the crystals in the bars that due to the expansion of bismuth upon solidifying the center of the bar is displaced upward forming a very peculiar funnel-shaped crystal.

24. **Performance of the graphic acoustic sounder during the Australian cruise of the U. S. fleet.** L. P. DELSASSO, University of California, Southern Branch.—By authorization of the Bureau of Engineering of the Navy Department, the device reported at a previous meeting was installed aboard the U. S. S. Maryland. Wherever the position of the ship could be fixed accurately it was found that the record obtained with the Graphic Acoustic Sounder was in good agreement with the charted depth. The device was found to operate satisfactorily from 20 to 3500 fathoms. It is shown that the shallow limit is fixed by the oscillator characteristics, while the maximum depth may be extended by the use of filters and greater amplification.

25. **Measurement of reverberation with the thermionic tube oscillator.** VERN O. KNUDSEN, University of California, Southern Branch.—The writer has made reverberation measurements, using an audio-frequency oscillator and a high quality loud speaking telephone receiver instead of a series of organ pipes as has been used by W. C. Sabine

and other investigators. The arrangement has the following advantages: (1) The acoustic energy generated by the receiver is proportional to the electric energy actuating the receiver, and therefore test tones of standard intensity are readily obtained from simple measurements of currents and impedances; (2) each standard test tone is based upon its tone of minimal audibility, the latter being determined by taking many measurements in different parts of the room, and therefore the reverberation measurements are almost independent of slight residual noises in a room, and do not require correction for the volume and absorption of the room; (3) the apparatus is more portable and convenient than the organ pipes with their auxiliary equipment. The apparatus has been used satisfactorily to determine the coefficients of sound absorption of many new materials used for the reduction of reverberation and noise in architectural interiors.

26. **An application of the Quantum Theory to the luminosity of diffuse nebulae.** H. Zanstra, National Research Fellow, California Institute of Technology.—It is well established, that galactic nebulae are emitting light under the influence of neighboring stars. Approximating the star by a black body and the nebula by a mass of pure hydrogen the following mechanism is worked out for the production of the nebular hydrogen spectrum. The ultraviolet star light beyond the head of the Lyman series is completely absorbed, causing ionization of the nebular atoms. The subsequent re-combination causes the re-emission of line spectra and continuous spectra. To account for the photographic intensity of the observed nebular emission spectrum produced under the influence of stars B_0 and Oe_5 (Hubble), we have to assign a temperature to those stars of about 33000°. This value is sufficiently close to temperature estimates from other sources (thermal ionisation). Further work is in progress, including a more refined temperature determination from the observed luminosity for the stars B_0 and Oe_5, and an application to planetary nebulae.

27. **Remarks on penetrating radiation.** Edward Condon, University of California.—An atomic model for Rutherford's "neutron" is presented which has an oscillation frequency closely corresponding to that estimated by Millikan from his recent measurements of the absorption coefficient of the radiation. A correction to the method of reducing the observations indicates that the absorption coefficient may be but half that given by the usual exponential law. The model used considers the oscillation of a proton inside an electron which has a volume distribution of electricity. The agreement of the frequencies observed and computed, is better than a 10% discrepancy.

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Webster, D. L.—No. 3.
Zanstra, H.—No. 26.
Zwicky, F.—No. 21.

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THE

PHYSICAL REVIEW

HIGH FREQUENCY RAYS OF COSMIC ORIGIN
II. MOUNTAIN PEAK AND AIRPLANE OBSERVATIONS

By R. A. Millikan and R. M. Otis

Abstract

The elimination in penetrating ray experiments of temperature and pressure effects is accomplished through *new features in the design of Wulf electroscopes,* but especially through immediate reduction in situ of all deflections to volts.

Variation of penetrating radiation with altitude and with time of day.—When suitable precautions are taken for eliminating the activity of adjacent rocks, both airplane and mountain peak observations agree in showing a definite variation of the penetrating radiation with altitude alone. Within the limits of experimental error all observations are consistent in showing no dependence of the penetrating radiation upon the time of day or upon the position of heavenly bodies.

Absorption coefficients of penetrating rays.—Absorption experiments made on Pikes Peak with lead sheets 4.8 cm thick furnish evidence for the existence on mountain peaks of copious new rays of local origin of no greater hardness than that of gamma rays. If these new rays are assumed to be homogeneous their absorption coefficient is about 3.1 per meter of water. These experiments, however, furnish no definite evidence for the existence of very penetrating rays of cosmic origin.

Necessary characteristics of cosmic rays if they exist—Such rays cannot produce as much as 2 ions per cc per sec. at sea level if they have an absorption coefficient not less than 0.25 per meter of water. If cosmic rays exist at all they must be less intense than this, or else they must be more penetrating than anyone has as yet suggested.

I. Introduction

THE sounding balloon experiments reported in Part I[1] had shown that the integrated natural leak of electroscopes at altitudes up to 15.5 km was slightly larger than the leak at the surface covering the same time interval. They had, however, shown nothing about the distribution of the leak with altitude, and they had shown nothing about the hardness of the rays causing the leak, further than to prove that if there were any rays of cosmic origin they must be very much more penetrating than had thus far been imagined in order to account for the smallness of the observed ionization. If, on the other hand, the small observed increase in ionization were due to radioactive materials in the atmosphere the penetrating rays should have the absorption coefficients of ordinary gamma rays.

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[1] Millikan and Bowen, Phys. Rev. **27**, 353 (1926).

In order to supply information upon these points a new group of experiments was planned and carried out in the summers of 1922–23. These involved (1) absorption experiments at the highest altitude to which we could transport considerable quantities of absorbing materials, and (2) experiments without absorbing screens in balloons, airplanes, and on mountain peaks to see whether altitude as such were a determining factor in the observed variations in the discharge rates, or whether there might be largely different discharge rates in different localities, thus accounting for the widely different results reported by different observers.

Suspecting, however, that these differences were due primarily to the failure to take suitable precautions against the influence of temperature upon the dimensions and elastic constants of the electroscopes, we adopted especial precautions for eliminating completely all such effects.

II. The Electroscope

The electroscope used is diagrammatically shown in Fig. 1 and a photograph of it inside a lead sheathing is reproduced in Fig. 3. This electroscope, which is of the Wulf type, was designed and constructed in the shops of the Norman Bridge Laboratory of Physics. Two quartz fibres of about 0.005 mm to 0.01 mm diameter and about 6 cm long, sputtered with platinum to make them conducting, are at the top soldered together into a small copper tube which is held by a set-screw in a brass cap, *A*, cemented to a long rod of quartz insulation. At their lower ends the fibres are fastened by a bead of shellac to a bow of unsputtered quartz fibre of slightly greater diameter. The ends of the bow are attached to brass pieces, *B*, whose effective lengths are adjustable, so that the fibres can be brought to the most efficient tension. This tension is one that will allow full-scale deflection when the electroscope is charged to the desired potential, but is still sufficient to make stable the fibres and to bring them together when uncharged. The screws for adjusting the tension on the fibres pass through an invar bridge which is supported in invar rods, *C*, which are in turn hung from approximately the same point in the top that supports the quartz insulator. Thus the tension is not changed by any deflection of the electroscope case due to a difference in pressure between the inside and the outside. Furthermore, inasmuch as the invar used was tested and ound to have a temperature coefficient of expansion practically equal to that of quartz, the tension of the fibres should be independent of temperature also. This was found to be the case.

The case of the electroscope was made from cylindrical brass tubing, 1.7 mm to 1.8 mm thick. The bottom was of brass, 5 mm thick, while the top was of rolled zinc and most of the metal parts connected with the top were turned from zinc castings. This case was air-tight under a pressure of 60 lbs. per square inch above atmospheric pressure. The enclosed air was kept dry by phosphorus pentoxide which filled the flat cylindrical box, *D*, at the bottom of the electroscope. This box, which is covered by a perforated top to keep the phosphorus pentoxide from being shaken out where it might cause trouble, screws onto a lug projecting from the bottom of the case.

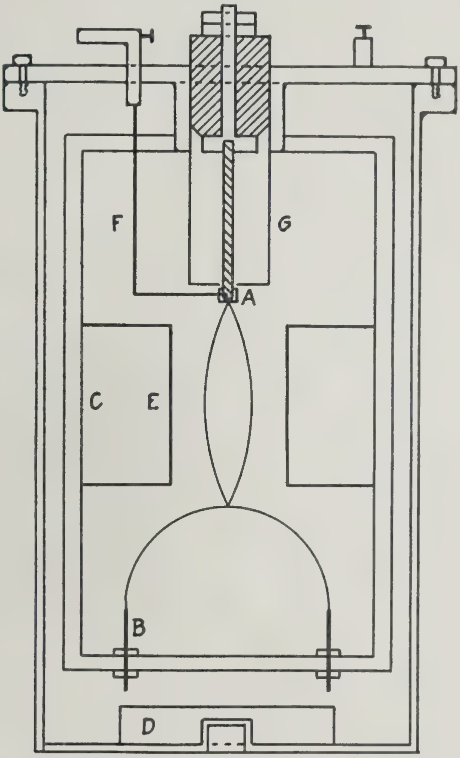

Fig. 1

The positions of the fibres were determined with the aid of a microscope having a scale in the eyepiece. A window on the opposite side of the case provided light. Sunlight was used when possible; in other cases a small flash-light bulb attached to a projection over the window was employed. The position of the objective as well as the eyepiece of the microscope could be varied, for the whole microscope fits into a tube, see Fig. 3, which extends into the case of the electroscope and terminates in a small glass window. This arrangement is very convenient because it is possible by simply removing the microscope to lower the electroscope into deep water without any protection and without fear of a leak. The fibres are kept in the focal plane of the microscope by the strengthened field due to the bent aluminum wires, *E*, projecting from the supporting invar rods. A very thick soft rubber gasket separates the top of the electroscope from the sides, so that the fibres could easily be swung into the center of the field of view by tightening the proper screws in the top.

The outside electrical connection to the fibres is made through the charging rod, *F*, which in the "on" position touches the brass cap to which the fibres are attached, and in the "off" position touches the case. This charging rod, as it passes through the case, is tapered at a very small angle to fit a greased ebonite bearing and is held tightly into contact by a strong spring.

A feature of the electroscope is that it is possible entirely to eliminate insulation loss if the loss across the thin quartz bow be neglected, and this is permissible because of the negligibly small diameter of the bow compared with the upper insulator. The quartz insulator is held in a brass rod which passes through an ebonite plug to the outside of the electroscope. This brass rod was held at the mean potential of the fibres throughout the period of observation thereby making impossible any insulation loss to the case. The brass rod and the quartz insulator are shielded from the rest of the electroscope by the shield, *G*, which is made in two parts, one of which may be rotated with respect to the other, leaving an opening to facilitate cleaning the insulator. The fact that the electroscope was designed with a view to accommodating lead screens accounts for the absence of projections from it and also for its small size. The volume was 1893 cc. The sensitivity varied in the different experiments from 1.4 to 2.1 volts per scale division. The capacity of the insulated system was found to be 1.32 cm.

III. METHOD OF OBSERVATION

Essentially what is done in making a measurement of the penetrating radiation is to charge the electroscope to a known potential and note the drop in potential of the insulated fibres in a given interval of time. Then from these data and the known capacity of the fibres together with the volume, *V*, of enclosed air in the electroscope, and the charge, e, on an electron, the rate of production of ions per unit volume can be calculated. Thus, the number of pairs of ions per cc per second which are formed is $C_f \Delta P / 3600 Ve$, where ΔP is the drop in potential of the fibres per hour.

However, the simple difference in the positions of the fibres as read on the scale is not an accurate measure of the potential drop of the fibres, especially after transportation of the electroscope from one place to another. Therefore, inasmuch as the electroscope was necessarily subjected to rather severe treatment, in order to destroy all doubt as to the meanings of the readings, the electroscope was calibrated before and after every period of observation, i.e., *the electroscope deflections were always reduced to volts at once and in situ.* This was easily and accurately accomplished by charging the electroscope to four known potentials in the region in which lay the reading to be interpreted. The four points thus obtained were plotted and a straight line was drawn through them. The four points almost always lay quite close to the line and it was never possible to make any large error. Such calibration at the time of reading is very essential to accurate results, for it was found that, while the sensitivity might not change appreciably, the whole calibration curve might from time to time move to the side, thereby changing the meaning in volts of a given deflection of the fibres. Also a slight change in focusing the microscope on the fibres of course changes the volt-value of the scale. These possibilities of error were completely eliminated by the method employed in these investigations.

The diagram of connections is shown in Fig. 2. When the switch S is in position 1, the battery is connected to the charging rod and to the case; when it is in position 2, it is connected to the guard ring on the quartz insulation and to the case. The 40,000 ohms resistance, R, is inserted in the electroscope circuit to avoid destructive currents if the charging rod should accidentally be brought into contact with the case while the switch S is still in position 1. Because no current flows through the electroscope, this resistance does not interfere with the measurement of potential.

The procedure in making an observation, then, is as follows: The charging rod is in the neutral position. The switch S is closed to position 1. The voltmeter switch is closed, a suitable potential is found on the battery, and the charging rod is connected to the fibres. The deflection of the fibres and the corresponding volts are then read as nearly simultaneously as possible. The charging rod is removed to neutral and a potential about 4 volts lower is found. The fibres are again charged and the deflection and volts are read. This is repeated until four comparisons between deflection and volts have been obtained. The fibres are then charged to a potential lying in the midst of the four potentials previously applied, the charging rod is brought to neutral, the switch *S* is lifted to the neutral position, and the charging rod is turned so that it touches the case. The deflection and the time are then observed. This deflection is afterward interpreted in terms of volts and gives the potential at the beginning of the period of observation. The potential is now adjusted to equal the mean value of the potential of the fibres to be expected during the period of observation, the voltmeter switch is opened, and the switch *S* is closed to position 2, thereby putting this potential on the guard ring at the top of the quartz insulator and making impossible insulation loss. This potential need not be adjusted accurately, because the insulation loss is probably negligibly small anyway. The guard ring was used only to make it impossible to criticize the results from the standpoint of insulation loss. At the end of the period of observation, the switch *S* is lifted to the neutral position, and the deflection of the fibres and the time are noted. The charging rod is turned to neutral and the process of calibration described above is gone through in order that the deflection just observed may be interpreted in volts. Suitable precautions were of course taken to insure saturation at all times and to permit the activity of the radium emanation to die out after changing the air in the electroscope.

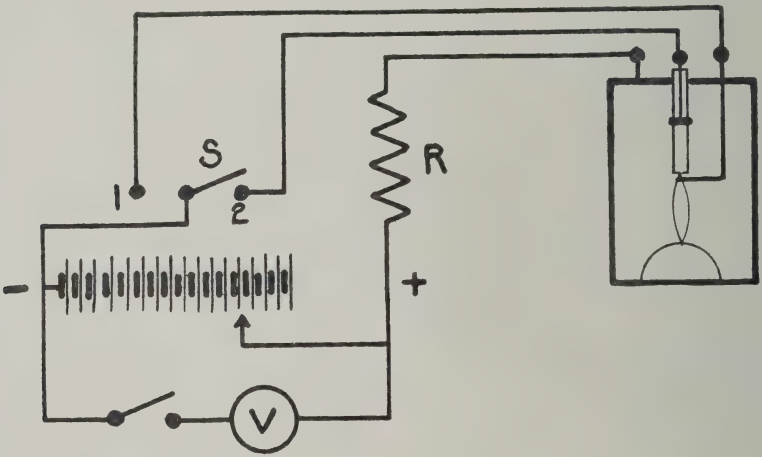

Fig. 2

IV. Measurements in Airplanes and Balloons

Preliminary measurements made in captive balloons at Ross Field, near Pasadena, by one of us (Otis) yielded results in agreement with those of other observers in that up to an altitude of 2000 meters the number of ions per cc per sec. was from 1 to 3 less than on the ground. No systematic change, however, was observed in this work at low altitudes.

The mean results of a long series of airplane flights made by Otis in 1922 at Marsh Field (near Riverside) and in 1923 at Rockwell Field (near San Diego) are shown in Table 1. These flights reached heights of more than 5000 meters. The numbers given are taken from a smooth curve drawn so as to fit as well as possible 17 observed points. In three instances these points depart from the curve by as much as 2.5 ions, out of a total discharge-rate, at the high altitudes where these points lie, of from 17 to 19 ions. The accuracy is limited by the shortness of the time, usually a half hour, during which a given altitude was maintained.

TABLE I

Airplane observations

Altitude	*Excess over ground*
500 meters	−2.1 ions/cc. sec.
760	−2.7
1200	−2.7
1750	−1.9
2500	−0.1
3400	+2.4
4200	+4.6
5200	+7.4

In these airplane flights the electroscope was suspended in front of the observer's seat by three pieces of ordinary laboratory rubber tubing, attached at their upper ends to the sides of the cockpit or to the gun-mount. The instrument was kept from swinging by another piece of tubing fastened at one end to a plug which screwed into the bottom of the electroscope and at the other end to the floor of the cockpit. The electroscope was thus made stable and free from the effect of vibration of the airplane motor.

The method followed was to go to the highest altitude attainable in a reasonable time, maintain the airplane accurately at that altitude during the period over which ionization was to be measured, then drop down to the next altitude, etc. Because of the limit to the amount of gasoline that can be carried to those high altitudes and the long time required to reach them, it was never possible to make observations at more than three different altitudes on the same day.

The results shown in Table I are in agreement with those of Millikan and Bowen[1] in that they show a markedly lower rate of leak at the highest altitudes reached than those reported by Hess and Kolhörster. However, as a whole these balloon and airplane measurements are in agreement with those of the European observers *in showing that the* *intensity of the penetrating radiation first decreases to a minimum after which it increases continuously with altitude.*

V. INDEPENDENCE OF PENETRATING RADIATION UPON TIME OF DAY

During three different summers, 1922, 1923, 1925, we have made long series of observations, not only at Pasadena but on Mt. Whitney and on Pikes Peak, to test the constancy of the ionization due to the penetrating rays. At Pasadena, where the average number of ions as measured by the foregoing unshielded electroscope is 11.6, the fluctuations may be as much as an ion, but no systematic variation whatever has been observed. On Pikes Peak, where the rate of discharge of the unshielded electroscope is nearly twice that at Pasadena no variation with time of day was found.

Table II gives in the first two columns a series of readings, each lasting two hours, taken on top of Pikes Peak inside a shield of lead 4.8 cm thick at the sides, 11 cm at the top, and open at the bottom, and in the last two columns a continuous series of twenty similar observations taken with the unshielded electroscope at altitude 4130 m on the trail to Mt. Whitney.

TABLE II

Observations showing independence of penetrating radiation upon time of day.

	Pikes Peak (4300 m) Shielded electroscope Mean time of observation	Ions per cm³ per sec.
9/22/23	2:43 P.M.	12.5
	4:57 "	12.4
	7:06 "	12.1
	9:26 "	12.7
9/23/23	11:31 A.M.	12.6
	1:38 P.M.	12.2
	4:05 "	12.8
	8:35 "	12.0
	10:45 "	12.0
9/24/23	12:57 A.M.	12.0
	3:25 "	12.2
	5:52 "	12.3
	Mean,	12.3

	Mt. Whitney Trail (4130 m) Open electroscope Mean time of observation	Ions per cm³ per sec.
9/16/22	8:50 P.M.	19.2
	10:58 "	18.9
9/17/22	1:05 A.M.	19.2
	3:12 "	18.9
	5:19 "	19.2
	7:26 "	20.0
	9:31 "	20.7
	11:37 "	19.4
	1:43 P.M.	18.6
	3:50 "	19.8
	5:59 "	19.2
	8:03 "	19.6
	10:07 "	19.3
9/18/22	12:12 A.M.	19.4
	2:18 "	19.8
	4:26 "	20.0
	6:33 "	20.4
	8:40 "	19.9
	10:49 "	20.0
	12:54 P.M.	21.0
	Mean,	19.6

The results shown in this table are merely typical of a very considerable amount of data, all of which is consistent in showing that within the limits *of our experimental error there is no dependence of the penetrating radiation upon daylight or darkness, or upon the position of any of the heavenly bodies. Two recent observations taken in a geological basin at a time when the Milky Way was wholly beneath the horizon gave no indication of a rate of discharge lower than that found when the Milky Way was overhead.*

VI. Dependence of Penetrating Radiation upon Altitude

As already indicated, the mean value of the penetrating radiations as taken by the unshielded electroscope on the Institute campus is 11.6 ions. At bench mark No. 15 of the U. S. Geological Survey on the Mt. Whitney Trail, altitude 4130 m it is 19.6. At bench mark No. 14, elevation 3660 m, the mean of two observations gave 17.3 ions. The last two observations were both taken on the granite rocks so that their difference, 2.3 ions, might be expected to represent a true altitude difference. *It is quite close to the difference shown in Table I in the readings taken in airplanes between the same levels.* Further, near bench mark No. 14 a shallow lake 1 m deep was found over which when the electroscope was floated on a raft the reading was 13.6, or 3.7 ions less than on the adjacent rocks. This difference is close to the mean of all the data heretofore collected on the change in electroscope reading in going from over land to over water. A collection of eight such differences taken by McLennan, McLeod, Kunsman, and Wulf is as follows: 3.3, 5.1, 3.8, 2.2, 4.9, 3.2, 3.8, 4.5; mean 3.8. This mean is in close agreement with the value of 3.7 here found. When 3.7 is subtracted from any of the aforementioned mountain observations they come fairly close to the readings at corresponding heights shown in Table I.

Although, then, the uncertainty due to variability in the activity of the adjacent rocks is great, *the evidence of all the foregoing mountain and airplane work is that there is a definite variation with altitude alone and that mountain and airplane observations can be brought into approximate agreement by suitable precautions for eliminating the activity of the adjacent rocks.*

VII. Absorption Experiments on Pikes Peak

None of our experiments so far had given us any information about the actual hardness of the penetrating rays. To obtain this information we constructed a completely encircling shield of seven sheets of lead, each a little less than 7 mm thick, the total lead shield having a thickness of 4.8 cm. The sides of the shield were made of semicylinders removable separately so as to open the electroscope to radiations from opposite directions. The top and bottom shields were circular plates of the same sheet lead.

In order to support this 300 pounds of lead it was necessary to use a steel frame consisting of two vertical rods supporting two ring-shaped plates. On the bottom plate rested the electroscope and the sides of the shield, while the top plate held the top of the shield. The bottom of the shield was placed on a steel strip and brought up to the bottom of the electroscope by nuts on the vertical rods. In Fig. 3 the electroscope is shown on its stand with part of the lead sheathing in place.

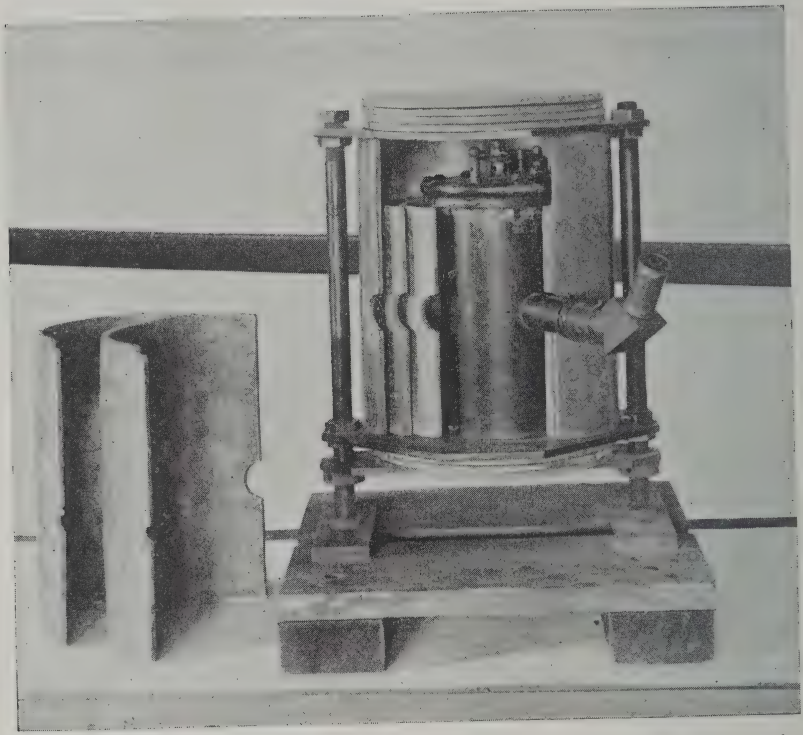

Fig. 3

Table III

Pike's Peak observations—out-of-doors.

A	Unshielded (mean of four one-hour runs)	23.2 ions per cm^3 per sec.
B	Shielded (4.8 cm of Pb.) (mean of four one-hour runs)	11.6
C	Top only unshielded (mean of three one-hour runs)	12.3
D	Bottom only unshielded (mean of four one-hour runs)	13.2
E	North side only unshielded (mean of four one-hour runs)	16.9
F	South side only unshielded (mean of four one-hour runs)	16.7
G	Both sides unshielded (mean of two one-hour runs)	20.55
H	On the tower (17 m high) of the building, unshielded, mean of two observations (17.1 and 17.5)	17.3

The results of all the observations taken on Pikes Peak are condensed into Tables III and IV. In Table III measurements *A* to *G* were taken out of doors on the rocks at the top of Pikes Peak. Measurement *H* was taken on the top of the skeleton steel tower above the inn. The measurements of Table IV were made inside the inn. The means of observations taken with the same apparatus in a tent on the campus of the Institute at Pasadena are given in Table V.

TABLE IV

Pikes Peak observations—indoors.

	Unshielded A	Shielded B	Top and bottom unshielded C	Bottom unshielded 16 layers on top D
		(Before the storm)		
	22.51	12.36	14.00	12.10
		12.23	15.04	12.60
		12.00	14.42	12.20
		12.63	14.54	12.80
Means	22.51	12.30	14.50	12.43
		(After the storm)		
	20.78	10.94	12.67	12.35
		11.11	12.70	11.75
			12.74	
			12.92	
			12.77	
Means	20.78	11.03	12.76	12.05

TABLE V

Pasadena observations

A	Unshielded	11.57
B	Shielded	9.37
C	Top only unshielded	9.54
D	Bottom only unshielded	9.40
E	Top and bottom unshielded	9.54
F	Both sides unshielded	10.75
G	Sides shielded, bottom unshielded, 16 layers of lead on top	9.28

There is no evidence in Table III of any difference in intensity of the penetrating radiations coming from the north and from the south, for the difference between the ionizations when the north side was unshielded and when the south side was unshielded is well within the limits of experimental error. The data show also that most of the radiation entered the electroscope through the sides, as was to be expected.

Another interesting result is that on Pikes Peak, the radiation out-of-doors was greater than that in-doors, while in Pasadena the radiation out-of-doors is a little over 1 ion per cc per sec. less than that in-doors in a concrete building. At Pasadena, then, the walls of the building add more radiation than they absorb from the outside, while on Pikes

Peak the reverse was true. This is doubtless because on Pikes Peak there is more outside radiation to absorb.

The radiation found on Pikes Peak is in substantial agreement with the measurements made at corresponding heights both on Mount Whitney and in airplanes. Thus, if the amount of radiation from the ground be taken the same as on Mount Whitney (3.7), then, following the same method as was used above, the radiation which would have been observed at the altitude of Pikes Peak (4300 m) if the ground had not contributed anything is, from the mean of all the A measurements in Tables III and IV, $22.2-3.7$ or 18.5 ions per cc per sec. The difference between this and that observed at Pasadena, from A, Table V, is $18.5-11.6$ or 6.9 ions per cc per sec. On referring to Table I it will be seen that this value fits reasonably well with the airplane data.

But it is obvious at once from Table III that there is a very much larger amount of soft radiation (of the hardness of gamma rays) on the mountain peaks than at Pasadena. Thus, while the difference between the shielded and the unshielded readings at Pasadena is but $11.57-9.37$ or 2.20 ions, on the Peak outdoors it is $23.2-11.57$ or 11.6^3, and when means are taken as above it is $22.2-11.57$ or 10.6^3. The rays producing these 11.63 (or 10.63) new ions found (unshielded) on Pikes Peak are necessarily soft rays since they are nearly all absorbed by the lead screen within which there are found all told but 2.23 more ions than at Pasadena. If these new rays found on Pikes Peak are assumed to be homogeneous, their absorption coefficient, α, computed from the relation $I=I_0e^{-\alpha d}$, comes out, since d, in meters of water, is $4.8\times 11.3 \div 100=0.54$,

$$\alpha=\log_e (11.63/2.23)\div 0.54=3.1 \text{ per meter of water.}$$

This indicates that these rays are but little harder than the gamma rays from RaC, which are taken by Kolhörster,[2] for example, as having a coefficient of 3.9 per meter of water, while for ThD $\alpha=3.3$. *In other words, a homogeneous radiation of about the hardness of the gamma rays from* RaC *or* ThD *would account for all the increase found inside and outside of lead screens in the Pikes Peak experiments. If the rays are not homogeneous, since, in any case 80% are absorbed in the lead, the great majority of them cannot be appreciably harder than gamma rays, and these must be of local origin since gamma rays are all absorbed in 500 meters or so of air.* The change from about 22 ions to 17.3 ions in going from the inn to the fifty-foot tower above it indicates that some of the new rays found on the Peak are softer than gamma rays.

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[2] Kolhörster, Sitz. Ber. d. Preuss. Akad. **34,** 371 (1923).

The foregoing evidence for the local origin of the greater part of the increased radiation found at the Peak is strengthened by a consideration of the effect of the storm noted in Table IV. This was a heavy snow storm, in which perhaps a foot of snow fell. The storm began at about six o'clock one evening and lasted throughout the night. About ten o'clock P.M. we noticed the reduction in the readings, a reduction which persisted during the hours during which we kept observing continuously after the storm. We had been observing day and night for two or three days before the storm, and had obtained a consistent series of readings throughout, so that the change surprised us greatly when it came. Table IV shows that all the readings, shielded and unshielded, are smaller after the storm than before. These readings were all taken indoors where the temperature was kept essentially constant, and no instrumental causes of the change could be found.

If these changes are due to the storm, i.e., to the blanketing of the earth with snow, they should be essentially the same in the column headed B as in that headed D. Taking, then, the mean of these two changes we obtain as the average shielded reading after the storm 11.5. The change under C, which is somewhat too large to be altogether consistent with the changes under A, B, and D, forces one to admit a somewhat larger observational or instrumental error of some sort than the general consistency of the readings otherwise indicates. Nevertheless, the readings as they stand, taking 11.5 as the mean shielded reading after the storm, show a drop due to the storm of about 8 percent for the unshielded condition and 7 percent for the shielded condition. When further we subtract from both readings the 6 or 7 ions which, according to our measurements made under water, were due to the radioactivity of the walls of the vessel and hence had nothing to do with external radiations at all, we see that the rays which get through the lead screen are cut down by the storm by quite as large a percent (apparently a slightly larger one) as the rays found in the unshielded electroscope. Such a result, if correct, *obviously requires the rays to be entirely of local origin.*

Both lines of evidence presented above point, then, to the conclusion that there is on mountain peaks a copious radiation of local origin and of a hardness not greater than that of the gamma rays of radium or thorium, but they reveal thus far no penetrating radiation of cosmic origin. If such a radiation exists at all it can at the most produce but a small part of the ionization observed in electroscopes on mountain peaks.

Kolhörster[3] in 1923 assumed such a radiation which produced 2 ions per cc per sec. at sea level, and had an absorption coefficient α in water of 0.25 per meter. Such a radiation would produce at Pikes Peak, where the average barometer reading is 17.5 inches, an ionization I_0 given by

$$\tfrac{1}{2}I_0 = e^{.25\times 4.3} = e^{1.08}$$

Therefore,

$$I_0 = 2\times 2.95 = 5.9$$

and of these 5.9 ions 5.15 would have been found inside our lead screen 4.8 cm thick. Similarly of the 2 ions assumed at sea level to be due to the cosmic rays 1.75 would be found inside the lead screen. That is, radiation of the assumed characteristics would have caused by itself inside our lead screen an increase of $5.15-1.75=3.4$ in taking the screened electroscope to the top of Pikes Peak even if none of the large increase in radiation shown by the unshielded observations on the Peak got through the lead—a supposition well nigh certain to be contrary to fact, for gamma rays from ThD would pass through this lead to the extent of about one sixth of the value outside.

The observed increase inside the lead screen and outdoors on the peak was, however, but 2.23 ions, that indoors after the storm but 2.13 and that indoors before the storm 2.9, a mean of 2.4 in place of the required minimum value of 3.4. In other words, penetrating cosmic rays of such characteristics as were assumed above cannot exist, since these rays alone, without the aid of any local radiation such as almost certainly exists, would produce on Pikes Peak a 40 percent greater increase in ionization inside the lead shield than we found. *The net result of the Pikes Peak work is, then, to establish quite definitely* (1) *the existence of a considerable increase in soft radiation in ascending from Pasadena to the Peak*; (2) *the non-existence of a radiation of cosmic origin of such constants as are supposed above.*

If cosmic rays exist at all they must be less intense at the surface than above assumed, or else they must be more penetrating than any one had as yet suggested.

Norman Bridge Laboratory of Physics,
California Institute of Technology,
March 1, 1926.

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[3] Kolhörster, Sitz. Ber. D. Preuss. Akad. **34,** 366 (1923).

JUNE, 1926 PHYSICAL REVIEW VOLUME 27

VARIATION WITH PRESSURE OF THE RESIDUAL IONIZATION IN GASES

By Wm. W. Merrymon

Abstract

The residual ionization in aged, dry, and dust free air, H_2, He, A, O_2, N_2, CO_2, CH_4 and C_2H_4 has been measured at pressures from 0 to 180 cm Hg. In order to reduce radio active contamination, a glass globe with a sputtered silver coating was used as the ionization chamber. An electrometer and compensation devices eliminated the effect of fluctuations in the battery and provided a null method that kept the guard ring at the same potential as the collecting system, thus eliminating leakage. The ionization curves show a more rapid rise in the lower pressures which ceases at from 15 to 65 cm Hg, when the alpha-rays causing it are absorbed. Above this the curves are straight lines. From these portions the increase in ions formed per cc per sec. per atm. has been determined. It is least in the case of hydrogen (2.033), and largest in the case of argon (18.59). This rate divided by the number of electrons in the molecule is approximately constant (0.855). The rather good agreement with Kleeman's beta-ray results might be regarded as an indication that the principal agency operative was of a beta-ray character.

Introduction

THE discovery about twenty-five years ago of the spontaneous formation of about 8 or 9 ions per cc per second continuously in air inclosed in sealed containers, called the residual or natural ionization, led to much work of investigation as to its properties—the effects of the kind of metal in the ionization chamber,[1] of the temperature,[2] as well as the change observed upon shielding by metals, water, etc.[3] These experiments showed conclusively that the observed effect at the surface of the earth was a composite one in which rays from radioactive substances in the ground, atmosphere, the building, and above all, radioactive contamination in the chamber itself, played a large part. McLennan and Murray[4] reduced the number of ions formed to only 2.6 per cc per sec. by using an ionization chamber made of ice on Lake Ontario when frozen over. Certain observations by Hess and Kolhörster in Europe and confirmed by Millikan and Bowen in America,[5] show an increasing rate of ion formation at high altitudes.

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[1] McLennan, Phil. Mag. **14,** 760 and 779 (1907); Phys. Rev. **26,** 526 (1908).

[2] Patterson, Phil. Mag. **6,** 231 (1903); Kingdon, Phil. Mag. **32,** 400 (1916).

[3] McLennan and Burton, Phil. Mag. **5,** 699 (1903);
Burton, Phys. Rev. **18,** 188 (1904);
Wright, Phil. Mag. **17,** 295 (1909).

[4] McLennan and Murray, Phil. Mag. **30,** 428 (1915).

[5] Wigand, Phys. Zeits. **18,** 445–463 (Sept. 15, 1924); Millikan and Bowen, Phys. Rev. **27,** 353 (1926).

This suggests a cosmical origin for a radiation of a penetrating power some seven times as great as any known radioactive rays. Swann[6] and others have considered theoretically the origin of a very penetrating radiation such as this supposed cosmical one, and he has also discussed the several results to be expected from such a primary ionizing source.

Most of the work done has been on air and at atmospheric pressure, although since the beginning of interest in the subject some observations have been made upon other gases,[7] principally hydrogen, carbon dioxide, and acetylene. Early observations showed that the rate of ion formation increased with the pressure, approximately proportional to it above atmospheric pressure. Recently Downey[8] and Fruth[9] have carried observations up to 75 atmospheres, and have found air, oxygen, and carbon dioxide to reach a constant value of ionization at about 50 atmospheres. Nitrogen, however, did not show this phenomenon although samples made by radically different methods were tried.

The purpose in the present work was to obtain a series of observations of the variation of the residual ionization with pressure in as many gases of an elementary kind as possible and under identical conditions. It was decided to try the use of an ionization chamber of glass with silver coating sputtered inside. By this means it was hoped to reduce the radio active contamination in the chamber, which is considerable in even the best metal vessels, and has been responsible for the distorted or discordant results of numerous observers. The nature of the chamber as constructed, particularly the stopper, limited the range of pressures from 0 to 180 cm of Hg.

Description of Apparatus

The general form and arrangement of the apparatus was suggested by Professor Swann, and is shown in Fig. 1. The parts C and D were used only in the auxiliary determination of the capacity-influence coefficient required for the computation. The switch K_c and the arrows from (5) in C to (1) indicate where the connection was made for these observations. During the taking of the regular data the small hole in the right-hand side of (3) was closed and the collecting system (1) was then entirely insulated and shielded. The ionization chamber G was a 5 liter, Pyrex, balloon flask with the neck cut off and ground down to the proportions shown. An auxiliary apparatus was used for sputtering the inside of the globe. The coating was quite uniform and of about 1/3 opacity over the globe, increasing to an opaque coat in the neck where electrical contact with the stopper had to be established. The central electrode or collecting rod in the globe was of glass and had also been sputtered with silver. It was attached by a brass rod inside it and a collar, to the stemrod which passed out through the stopper. Contact between the silver coatings of globe and rod, with the brass stopper and stem, respectively, were made with pieces of tinfoil. The arrangement of the guard ring in the stopper and of the gas inlet tube (*p*) were as shown.

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[6] Swann, Phil. Mag. **47**, 306 (1924); Bull. Nat. Research Coun. No. 17, p. 66 (Mar., 1922).

[7] Jaffe, Phil. Mag. **8**, 556 (1904); Ann. der Physik (2) **28**, 326 (1909);
Wilson, Phil. Mag. **17**, 216 and 321 (1909);
McLennan and Trealeaven, Phil. Mag. **30**, 415 (1915).

[8] Downey, Phys. Rev. **16**, 420 (1920); **20**, 186 (1922).

[9] Fruth, Phys. Rev. **22**, 109 (1923); Broxon, Phys. Rev. **27**, 542 (1926).

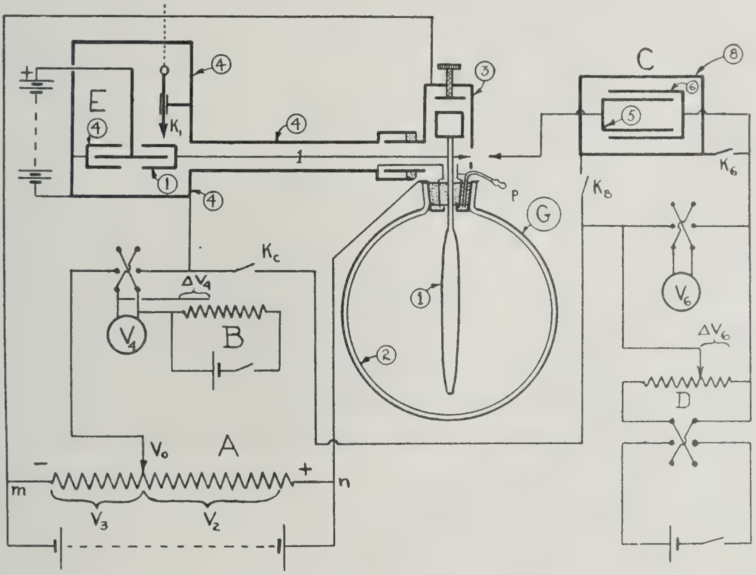

Fig. 1. Diagram of apparatus.

The upper end of the stem of the collecting rod was enlarged into a cylinder that fitted the cap (3) closely. This provided the auxiliary capacity for the compensation scheme suggested by Swann[10] for such observations. The disk in the top of (3) could be screwed down to adjust this capacity, and the point V_0 on the high resistance in *A* was varied until $V_3C_3=V_2C_2$. The various capacities then compensate in their action and there is no inductive deflection of the needle due to fluctuations of the battery in *A*. The balance was subsequently maintained throughout the work by moving V_0 slightly, as required, so that the electrometer needle would deflect only a few millimeters upon throwing on or off the battery in A. The cap (3) was held by a hard-rubber collar (not shown) that fitted on the outside of the guard ring.

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[10] Swann, Phys. Rev. **17**, 240 (1921).

The high resistance in A was made by winding IAIA No. 40 wire on paper-wrapped sections of brass tubing 3/8 by 9 inches long (1×23 cm). The total resistance of the 104 tubes used was 101,000 ohms. The resistance B was a cranking resistance of about 28 ohms used with a dry cell. The battery on the needle was a 100-volt silver-chloride set, as described by Erikson.[11] The battery in A was a 220-volt set of dry cells. Throughout the observations the point V_0 was such that V_2 was 178 volts, and V_3 was about 42 volts.

The electrometer was an ordinary Dolezalek instrument at a sensitivity of 1,000 mm per volt on a scale 130 cm distant. The whole of the apparatus was mounted on a large brick pier and, except for the part A, it was completely insulated from the pier by various plugs of sulfur to eliminate leakage between the parts. The insulating material in the stopper of the globe was of hard-rubber.

Method of Making Measurements

Usually the positive terminal of A was attached to the globe, and the collection of charge by the central system would raise its potential with respect to the other quadrant and case. By cranking B the potential of the case was raised ΔV_4 volts and so kept up to that of the collecting system, thus providing a null method. It is to be noted that by this method the potential of the collecting system and guard ring in the stopper were always the same, and hence leakage between them was practically eliminated.

Having brought the system to balance by suitable adjustment of the point of contact V_0, the taking of observations consisted in raising key K_1, bringing the spot of light to the zero point by cranking B, taking the starting time and initial reading V_4. As the charge collected the spot was held on the zero position by cranking B, and every few minutes a reading of the time and voltage on V_4 was made. The readings were continued in this way usually from 20 minutes to an hour, depending on the gas and pressure. During this interval a number of readings of time and V_4 would be made and the separate rates of leakage calculated. The accuracy attained was such that the series of results usually agreed among themselves to within a few hundredths of an ion per cc per sec.

Throughout the making of an observation,

$$V_1 = V_4 = V_0 + \Delta V_4.$$

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[11] Erikson, J.O.S.A. and R.S.I. **8**, 549 (Apr., 1924).

At the start

$$Q_1 = c_{11}V_0 + c_{21}(V_0+V_2) + c_{31}(V_0+V_3) + c_{41}V_0.$$

At the close

$$Q_1 + \Delta Q_1 = c_{11}(V_0+\Delta V_4) + c_{21}(V_0+V_2) + c_{31}(V_0+V_3) + c_{41}(V_0+\Delta V_4).$$

Hence,

$$\Delta Q_1 = (c_{11}+c_{41})\Delta V_4.$$

Let q represent the number of pairs of ions formed per cc per second, Since

$$dQ/dt = \text{const.}\, dV/dt = (c_{11}+c_{41})\Delta V_4/t,$$

then

$$q \times G \times 4.774(10)^{-10} = (c_{11}+c_{41})(\Delta V_4/t) \times (1/300).$$

where G is the volume of the globe (5350 cc) and t the time in seconds since the start. As indicated below, the capacity-influence coefficient

$$(c_{11}+c_{41}) = 27.97 \text{ e.s.u.}$$

Therefore,

$$q = 3.65(10^4) \times \text{volts cranked in per second.}$$

The gases were introduced very slowly into the globe, usually up to the limit of pressure, and observations were made. Then the pressure was reduced a few centimeters and another observation was made; and so on for the series.

SUBSIDIARY MEASUREMENTS

It is very necessary in these observations to make sure that saturation voltages are used, and therefore preliminary observations were carried out which showed that a battery of 220 volts, which was used throughout the work, gave complete saturation. Trials were made with both the positive and negative end of the battery in A connected to the globe, and it was found that there was a constant slight difference between the two sets of results, the direction dependent upon the sign of the potential on the needle. This was due to the quadrant of the electrometer acting as an ionization chamber so that when the needle was positive and the positive terminal of A was on the coating of the globe, the resulting ionization observed was about 0.7 ion larger than when the negative terminal was attached to the coating. This was true throughout the range of pressures. The needle was kept positive throughout the observations here reported, and the coating was positive.

The cap (3) also acts as an ionization chamber and drives to the collecting system ions of sign opposite to those being collected in the globe. This together with that from the electrometer quadrants is practically constant throughout any one set of readings, depending, of course, upon the atmospheric conditions. Of these two, the effect due to the cap is the larger and the two together constituted an extraneous current which opposed the charge being collected in the ionization chamber. At low pressures this becomes predominant. It is equal to the value of the ionization observed at zero pressure.

To test for this extraneous current, an observation would occasionally be made with the wire from *n* to the globe disconnected, and a wire from the negative terminal *m* joined to the coating. The extraneous current is one-half the sum of the current obtained by this connection and that as normally observed. Repeated observations throughout the range of pressures gave a constant result which agreed very closely with the current observed at zero pressure. Therefore, for determining the absolute values one seems warranted in supposing the curves raised until they terminate at zero ions with zero pressure. They have, however, been plotted just as observed, according to deflections to right or to left. The pressures are in centimeters of *Hg* and the ordinates show the number of pairs of ions formed per cc per second.

For the determination of the capacity-influence coefficient $(c_{11}+c_{41})$ the parts C and D of the apparatus were used. The condenser C was a Gerdien variable standard made by Gunther and Taegetmeyer and provided with calibration curves for both induction and capacity coefficients. When the shield (8) was connected to the electrometer case for observations, the influence coefficient c_{65} was involved. This was read from the calibration curve of the instrument for the particular setting used. With the shield connected to the outer coating (6) the capacity coefficient c_{55} was employed, and this was likewise scaled off from the other calibration curve. Both methods of connection were used for several settings of the instrument. The results agreed very closely throughout the range of pressures. The observation was made by raising K_1, then quickly introducing a fraction of a volt ΔV_6 and compensating the resulting deflection of the electrometer by cranking B. This method eliminated the effect of contact potential and hence the results were not influenced by the direction of the battery in D. The ratio of ΔV_6 to $\Delta V_4 \times c_{65}$(or c_{55} for the second method) gave $(c_{11}+c_{41})$. The average value was 27.97 e. s. u.

RESULTS

The results of the observations are shown in Figs. 2, 3, 4, and 5. The gases used were from pressure tanks which had stood for at least one month so that the emanation content should have decayed to a negligible value. The gases were introduced into the evacuated globe through a long P_2O_5 drying tube and a similar tube filled with absor-

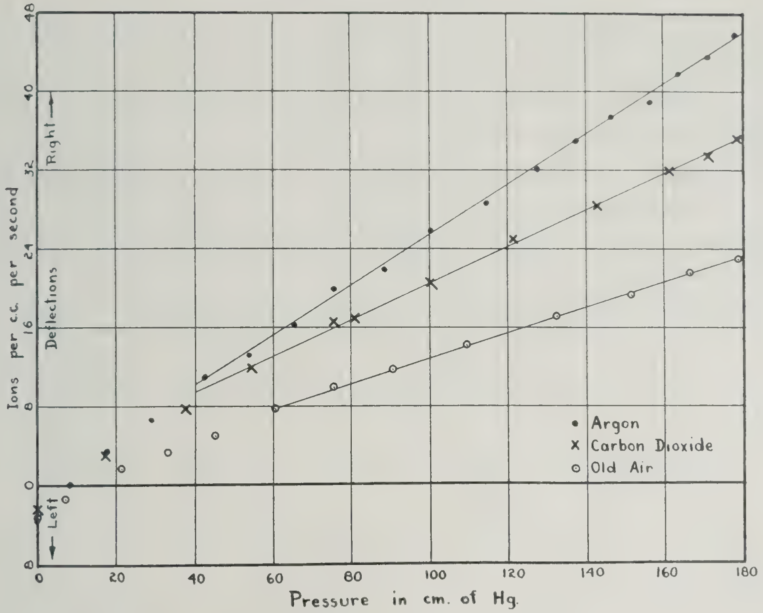

Fig. 2. Variation with pressure of the residual ionization in argon, carbon dioxide and old air.

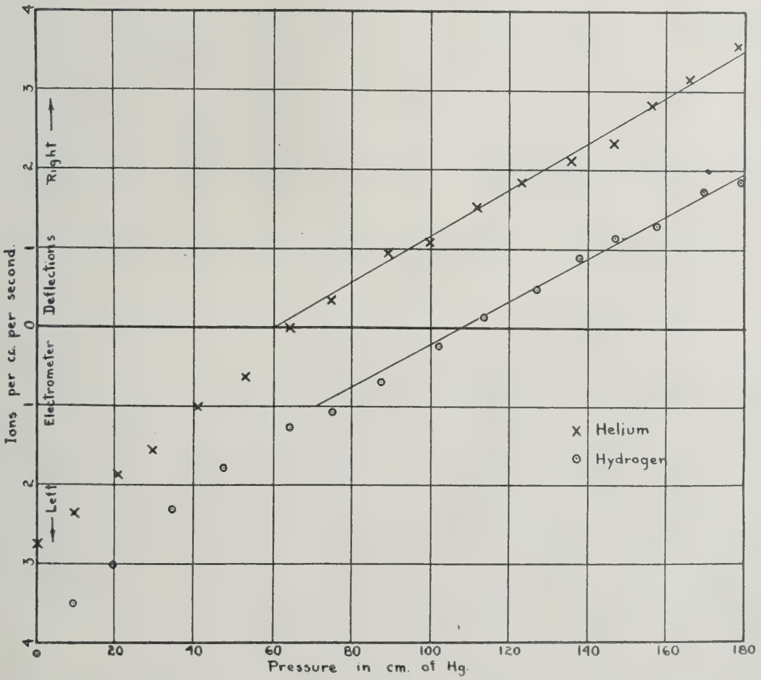

Fig. 3. Variation with pressure of the residual ionization in helium and hydrogen.

bent cotton to remove dust. With these precautions subsequent observations were found to agree to within the error of observation, about 0.2 ion per cc per second. In some cases the gases were left in the apparatus for weeks to see if they would show any decrease in activity, but none was found. Neither was there any increase in activity following their introduction. The observations could be stopped at any point and subsequently taken up and carried on again. The curves could be repeated, and many of them were taken two or three times.

The argon of Fig. 2 was held in the tank several months before use. The carbon dioxide was from the usual pressure tanks, and was known to be at least six months old. The old air was from a pressure tank that had been filled with dry, dust-free air five months previous to its use. The helium and hydrogen of Fig. 3 were from tanks that had been on hand for many months; the same is true for the oxygen and nitrogen of Fig. 4. As a check experiment, the helium and hydrogen were run through charcoal and spiral tubes immersed in liquid air, but no change in the results as compared with the former ones was found. The ethylene shown in Fig. 5 was known to be several months old, and the methane was at least six weeks old. The air from liquid air was obtained by placing some fresh liquid air in a Pyrex stoppered tube with side neck to lead off the evaporating air. The lower part of the tube was put

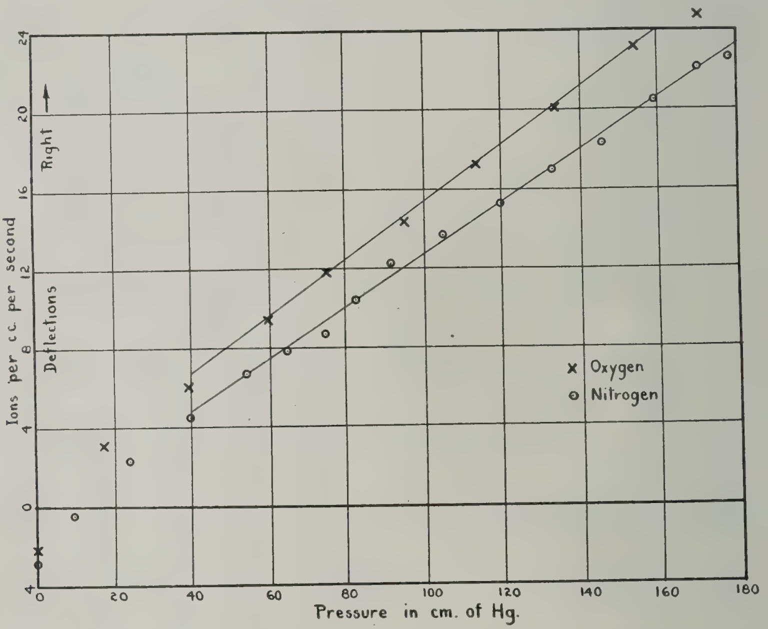

Fig. 4. Variation with pressure of the residual ionization in oxygen and nitrogen.

down into a flask of liquid air. As some of the air evaporated, it was led into the globe through the drying tubes. The results fulfilled the hope that air could be gotten at once that would behave like well aged air, as far as emanation is concerned, for any present should remain behind in the liquid state.

The numerical values of the results are given in Table 1. As above, q represents the number of pairs of ions formed per cc per second, and in column 2 the increase in q per atmosphere increase in pressure is given. In column 3 the value of q at atmospheric pressure is tabulated, and to facilitate comparisons this is given in column 4 on the basis of that for air = 100. Columns 4 to 8 incl. are for relative ionization at atmospheric pressure. Column 5 contains data from an early paper by C. T. R. Wilson[12] for the residual ionization in different gases. The data of column 6 for the natural ionization observed in the laboratory, and of column 7 for the ionization produced by alpha-rays are from a paper by McLennan and Trealeaven.[7] Column 8 contains data from a paper by Kleeman[13] for the relative ionization produced by beta-rays in different gases, and in this the values for nitrogen, methane, and ethylene were

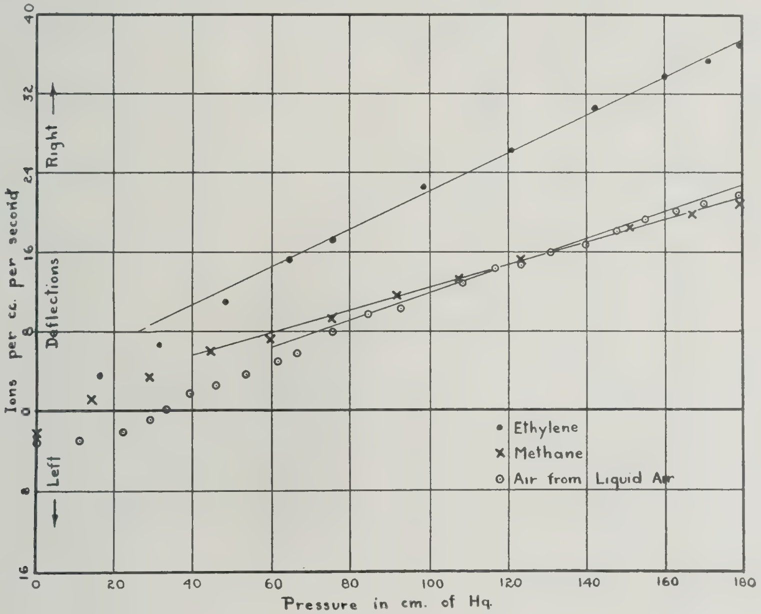

Fig. 5. Variation with pressure of the residual ionization in ethylene, methan and air from liquid air.

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[12] Wilson, Proc. Roy. Soc. **69,** 280 (1901).

[13] Kleeman, Proc. Roy. Soc. A. **79,** 231 (1907).

computed from the atomic ionizations as given in his table. This is in substantial agreement with similar data in a paper by R. J. Strutt[14] as well as in the above paper by McLennan and Trealeaven, although the data given for alpha-rays by the former authors differ rather pronouncedly from that of McLennan and Trealeaven, which was written a number of years later and has therefore been selected.

TABLE I

			Relative ionizations, air = (100)					
Gas	dq/atm	q at 76 cm	q for air = 100	Wilson	Mc L. and Treal.	Alpha-rays	Beta-rays, Kleeman	$\frac{dq/\text{atm}}{\text{electrons}}$
H_2	2.033	5.0	41.0	18.4	22.6	56.0	16.5	1.016
He	2.215	3.2	26.2	.....	.....	.....	.....	1.108
CH_4	8.68	12.5	102.5	.....	.....	.....	118.0	.868
N_2	10.00	12.0	98.3	.....	.....	.....	95.0	.714
C_2H_4	14.70	20.2	165.5	.....	139.7	113.3	164.0	.919
Air	9.88	12.2	100.0	100.0	100.0	100.0	100.0	.707
O_2	10.95	14.2	116.4	.....	.....	.....	117.0	.685
A	18.59	22.8	187.0	.....	.....	.....	.....	1.033
CO_2	14.22	19.6	160.6	169.0	114.3	80.4	160.0	.647
								Mean = 0.855

DISCUSSION OF RESULTS

Effects from radioactive contamination in the walls and floors of a laboratory building can scarcely be avoided altogether, but it was believed that any such effects in these observations would be constant within the range of pressures used, and subsequent observations indicated that they were, at least within the error of observation. The effect of a trace of radioactive contamination within the ionization chamber itself would most probably be largely due to alpha-rays, but possibly also to beta-rays. The alpha-rays would be absorbed at less than one atmosphere in a chamber of the size used. The effect would therefore be to produce a current increasing proportionately with the pressure above vacuum until the rays completed their paths in the inclosed gas, and thereafter, a constant additive factor. The increased curvature in the lower parts of the curves is attributed to this cause, as has been done by G. Jaffe[7] in the case of his curves, and also by Downey.[8] The slope of the curves has been determined from their upper straight portions.

From a consideration of the curves it appears that in the case of each of the gases under residual ionization the increase per atmosphere of ion formation is characteristic of the gas in question, and is constant up to the limit of pressures employed. The attempts of some investigators[12] to relate this phenomenon to the density of the gases were not successful. That there is a close connection between the ionization in different gases and their electronic configuration has suggested itself. Found and Dushman[15] from their studies with the ionization gauge have felt that their observations indicated a quantitative relation between the ionization in different gases under electronic bombardment and the number of electrons in the molecule, or "molar number." There is entered in column 9 the increase in the residual ionization per atmosphere divided by the number of electrons in the molecule, assuming 14 for air. The results, although by no means of close uniformity, are at least suggestive. Hydrogen, the noble gases, and the heaviest one, carbon dioxide, depart the farthest from the mean, the former being 20 to 30 percent high and the latter 24 percent low.

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[14] Strutt, Proc. Roy. Soc. A. **72**, 209 (1903);
Marx, Handbuch der Radiologie, Vol. I, p. 37; Vol. II, p. 40.

Found and Dushman observed their results with hydrogen and helium to be higher than would be expected on such a basis, but their results for argon and carbon dioxide are not abnormal. Kossel[16] also found that the secondary ray production in hydrogen by electrons of 1000 volts was abnormally large, and that hydrogen retained this peculiarity when in combination. The data in column 9 likewise show methane and ethylene to be above the mean, but the differences suggest that the chemical bonding may also be a factor. Although the energy necessary to knock an electron from various atoms and from different parts of the same atom varies greatly, yet as a modifying condition may be mentioned Bohr's conception, "of the penetration, in the case of the less simple atoms, of electrons of highly elliptical orbits into the region inside the shells of lower quantum number, giving these penetrating electron orbits in some cases a smaller mean potential energy and therefore a higher stability, than some of the orbits corresponding to smaller quantum numbers."

If the ionization produced by the earth's penetrating radiation is to be compared to electronic ionization, it seems probable that it should be with that of high speed electrons. It may be of interest, nevertheless, to note that Hughes and Klein,[17] Jesse,[18] and Compton and Van Voorhis[19] using electrons of low velocity for producing ionization, do not

[15] Dushman, "High Vacua," p. 121;
Found and Dushman, Phys. Rev. **23,** 734 (1924).

[16] Kossel, Ann. d. Physik **37,** 393 (1912).

[17] Hughes and Klein, Phys. Rev. **23,** 450 (1924).

[18] Jesse, Phys. Rev. **26,** 208 (1925).

[19] Compton and Van Voorhis, Phys. Rev. **26,** 452 (1925).

find their results to support Dushman's suggestion as a quantitative relation. In Jesse's results He, A, CO, and N_2 would be practically together on the basis of the number of electrons in their molecules, but Ne was about 60 percent below and CH_4 and H_2 about 45 percent and 90 percent respectively above the mean of the first four. However, as suggested by Compton and Van Voorhis, it may be that the Dushman relation is more accurate at higher voltages—as might be expected on theoretical grounds and as is indicated by the work of Kossel, who made the same suggestion on the basis of his measurements at 1000 volts. McCallum and Focken[20] found that the increased ionization with higher voltages is much larger in neon than in the diatomic gases, hydrogen and nitrogen. The effect of higher accelerating potentials in increasing the ionization in neon relative to the others is also evident in Jesse's data.

Downey[8] and Fruth[9] found that the variation in the natural ionization of gases with pressure obeys a linear law up to more than 20 atmospheres, and they give the increase in ionization for air as from 1.23 to 1.58 ions per cc per sec. per atmosphere increase in pressure. The increase per atmosphere for air as observed here is much larger than they report. This might be explained as due to a beta-radiation within the chamber, or gamma-rays from the walls of the room. However, it is about the same proportion of the value at one atmosphere as was observed by McLennan and Burton.[3] Judging by Fruth's curves for O_2 and prepared N_2, his increase for O_2 is about 1/10 greater than that for N_2, which proportion agrees with the data in column 3 of the table. The value of q obtained for air at atmospheric pressure is about the same as Downey and Fruth observed, and lies between those for O_2 and N_2. McLennan and Murray[4] observed 7.6 ions with the best zinc chamber in buildings entirely free from contamination. The same chamber gave only 4.65 ions per cc per sec. on the ice over Lake Ontario. This indicates the degree of influence to be expected even in selected buildings.

The experimental curves agree in general with those of C. T. R. Wilson[12] for the spontaneous ionization in several gases. His vessel was smaller, and his curves do not all extend even to atmospheric pressure. He also noted the decrease in slope of his curves at pressures approaching one atmosphere, but regarded the significant part of his curves as that below this point.

The fact that the data of column 6 is uniformally lower than that of column 4 would suggest that the location in which McLennan and

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[20] McCallum and Focken, Phil. Mag. **49**, 1318 (1925).

Trealeaven made their observations had greater freedom from radioactive contamination. It is also true that in the case of both H_2 and He the presence of small amounts of other gases affect the ionization to a relatively greater extent. This might account for the apparently high value for H_2 in column 4.

The ionization for beta-rays and gamma-rays is about the same for the lighter gases, but for the heavier gases the gamma-ray ionization becomes much larger than that for beta-rays, because of secondary radiation of the beta and gamma type from the walls of the vessel and from the gas. Ionization with alpha-rays, as indicated in column 7 is quite different from the others; the ionization in H_2 is much greater, and in CO_2, C_2H_4 and N_2O considerably less, than that for the natural ionization or for beta-ray ionization. The somewhat better agreement between columns 4 and 8 might be taken as an indication that the residual ionization as observed is due chiefly to the effects of a radiation of a beta-ray character. It might be objected that comparisons with beta-rays should be made not of q but rather dq, since q involves alpha-rays. However, the beta-ray data quoted did not give values of dq, and furthermore, it seems probable that they also involved alpha-ray contamination to at least as great an extent as in the case of these observations.

The use of a glass vessel with sputtered coating (aside from the limitation it may place upon pressure) appears to be an advantage, and it would be of interest to employ vessels of different coatings particularly ones more resistent to active gases. It would be desirable for the vessel to be larger than this one and capable of standing several atmospheres pressure.

In conclusion the writer wishes to acknowledge his indebtedness to the members of the Ryerson Faculty, particularly to Professor W. F. G. Swann who initiated the work and method, and to Professor A. J. Dempster for his suggestions and the direction of the research during the last year. The observations here reported were made prior to June, 1925.

Ryerson Physical Laboratory,
University of Chicago,
December 30, 1925.

NOTE ON THE DECAY OF RaE*

By L. F. Curtiss†

Abstract

The decay of the activity of a preparation of RaE shown to be quite free from RaD has been observed over a period of 45 days. The *half period*, determined by the method of least squares, for this sample was 5.07 days. This value agrees with measurements by Antonoff, Meitner, and Bastings, but it is in disagreement with the value of 4.85 days determined by Thaller and recently observed by Fournier. It appears that the value given by Thaller, and previously accepted, cannot be correct.

SINCE 1912 the value 4.85 days has been accepted for the half period of RaE, based on measurements by Thaller.[1] Recently Bastings[2] redetermined the half period and found a value considerably higher. The mean of measurements on several sources gave 4.98 days. The latter determination however has been questioned by Fournier,[3] who observed the activity of three different sources and concluded that the value given by Thaller is correct. Obviously it is desirable to know the rate of decay of RaE with greater certainty than this disagreement permits.

In order to investigate this question, I have prepared a source of RaE and have observed its activity over a period of several weeks. Of course it is important to obtain a source as free as possible from RaD, the parent product. The RaE was obtained electrolytically on a platinum electrode from a RaE solution prepared from old radon tubes.± Conditions were adjusted so that the RaE should go to the cathode. The deposit was tested for RaD by exposing in a beta-ray spectrograph with the field properly adjusted to throw the RaD spectrum on the plate. A twelve hour exposure gave a very faint trace of the strong RaD line whereas an exposure of about three hours with the anode from the above electrolysis gave the complete spectrum. The deposit was then dissolved from the cathode by dilute HCl and the RaE obtained by rotating a nickel disk for about thirty minutes in this solution. Since little RaD was present in this solution we might expect the nickel disk to be fairly free from it. Measurements of the residual activity of the source after fifty days proved this to be the case, as is indicated in the table. The nickel disk was mounted 15 cm below the face of a beta-ray electroscope as shown in Fig. 1 at *S*. It was left in position throughout the observations. A shutter *B* of lead 3 mm thick could be introduced in order to determine the natural leak from time to time. The foil *F*, in the lower face of the electroscope, was of aluminum 0.060 mm in thickness. Careful observations of temperature and of barometric pressure made it possible to reduce all readings to standard conditions. Table 1 gives the readings obtained, corrected for natural leak, temperature and pressure. It will be seen that at the end of 45 days the activity had become practically zero, indicating that very little RaD is present.

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* Published by permission of the Director of the Bureau of Standards, Department of Commerce.

† National Research Fellow.

[1] R. Thaller, Wien Ber., **121**, 1611 (1912).

[2] L. Bastings, Phil. Mag. **48**, 1075 (1924).

[3] G. Fournier, Comptes Rendus **181**, 502 (1925).

± I wish to thank Dr. Lind of the Fixed Nitrogen Laboratory for supplying this material.

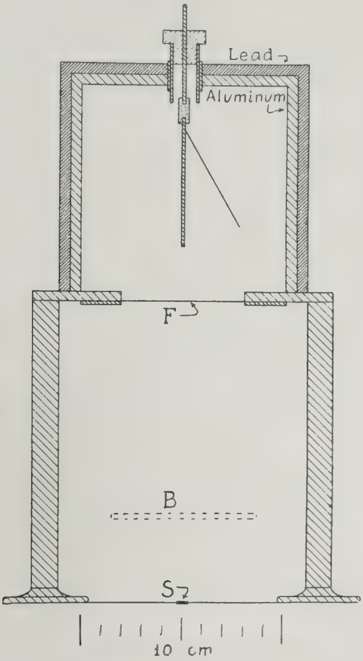

Fig. 1. Beta-ray electroscope.

TABLE I

Decay of activity of RaE

Hours	I	$\text{Log}_e\, I$	Hours	I	$\text{Log}_e\, I$	Hours	I	$\text{Log}_e\, I$
0.0	42.5	3.749	126.3	20.1	3.000	264.0	9.4	2.241
20.0	37.1	3.617	139.8	19.0	2.939	288.9	8.1	2.092
22.4	36.8	3.605	165.5	16.5	2.803	314.5	6.5	1.872
42.8	33.2	3.502	187.0	14.8	2.694	345.25	6.0	1.792
70.0	28.6	3.353	213.6	12.4	2.517	1080.	0.06	.....
91.8	24.7	3.206	244.0	10.4	2.341	....	....	.....

The results are shown graphically in Fig. 2 where the logarithm of the observed activity has been plotted against the time. The slope has been determined by the method of least squares. This calculation gives a half period of 5.07 days. The values obtained by Bastings for different sources were as follows: 5.04, 4.96, 5.02, 5.02, 4.98, 4.97, 4.96. It is evident that my observation agrees fairly well with his measurements and cannot be reconciled with Thaller's determination, or with that by Fournier. It may be well to recall that for various preparations Thaller obtained half periods ranging from 4.6 to 5.0 days and that presumably the accuracy of his measurements was not very high. The value 5.0 days has also been observed by Antonoff[4] as well as by Meitner.[5] The evidence thus far seems to favor a half period much nearer five days than that heretofore accepted. The value given by Bastings may rather be too low than, as Fournier states, too high.

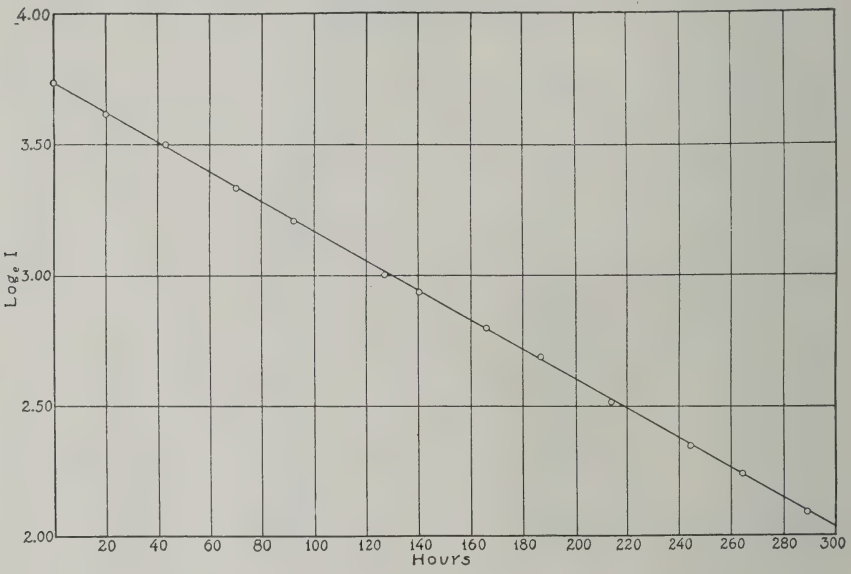

Fig. 2. Curve showing variation of the logarithm of the activity with the time.

Of course the writer is aware that the value reported here may well be too high. However it is difficult to see how, in view of the precautions taken and the consistency of the observations, it can be in error by more than 1 percent. Even granting that the error may be as great as this, there is still no possibility of agreement with Thaller's value. Further work is in progress.

Bureau of Standards,
Washington, D. C.
February 15, 1926.

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[4] Antonoff, Phil. Mag. **19,** 825 (1910).

[5] L. Meitner, Phys. Zeits. **12,** 1094 (1911).

JUNE, 1926 PHYSICAL REVIEW VOLUME 27

THE RATIO OF THE MODIFIED TO THE TOTAL SCATTERING COEFFICIENT OF X-RAYS

By O. K. De Foe

Abstract

Use has been made of the fact that the modified portion of scattered x-rays has not only a greater wave-length but also a greater absorption coefficient than the primary x-rays in order to separate the modified and unmodified portions of a scattered x-ray beam. The method involves the change in the intensity of scattered x-rays when a given thickness of aluminum is transferred from the primary to the scattered beam. Using a balance method, measurements of the ratio of the modified to the total scattering coefficient have been made for x-rays of wave-lengths 0.27A to 0.58A scattered from carbon, aluminum and copper at angles varying from 60° to 130°. *Comparison with theory.* Jauncey's theory predicts that the ratio should become unity when vers $\phi=242\lambda_0^2/\lambda_s$ (λ_s and λ_0 being measured in Angstroms). For carbon at 60° and 90° the experimental ratio becomes unity at wave-lengths of 0.32A and 0.46A respectively: The theory gives 0.31A and 0.44A respectively. A calculation of the modified scattering coefficient for copper at 90° for $\lambda=0.4$A gives $0.71s_0$ (where s_0 is the Thomson coefficient at 90°), while the theory gives $0.74s_0$. Thus as far as they go the experiments are in agreement with the theory.

1. Introduction

A. H. COMPTON[1] has shown theoretically that x-rays scattered at an angle should be changed in wave-length by an amount given by the formula

$$\lambda_\phi-\lambda_0=h/mc \text{ vers } \phi = .024 \text{ vers } \phi \tag{1}$$

This value is derived on the ssumption that the electrons which do the scattering are free and at rest. Experiments by Compton,[2] Ross,[3] and others confirm this result but show also unmodified scattering which the theory does not predict. The existence of the unmodified line necessitates the definition of two scattering coefficients, one for the modified and the other for the unmodified portion. Previous determinations of the scattering coefficients give approximately the sum of these two coefficients. Throughout this article we shall denote by σ_1 and σ_2 the spherical linear scattering coefficient for the unmodified and modified x-rays respectively; while s_1 and s_2 will be used to denote the linear scattering coefficient per unit solid angle in the direction ϕ with respect to the forward direction of the primary rays for the unmodified and modified x-rays respectively. If the primary x-rays are unpolarized the quantities σ_1 and s_1 are connected by the relation

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[1] A. H. Compton, Phys. Rev. **21,** 483 (1923).

[2] A. H. Compton, Phys. Rev. **22,** 408 (1923).

[3] P. A. Ross, Proc. Nat. Acad. Sci. **9,** 246 (1923); **10,** 304 (1924).

$$\sigma_1 = \int_0^\pi 2\pi s_1 \sin\phi \, d\phi \tag{2}$$

while a similar relation exists between σ_2 and s_2.

Jauncey[4,5] has proposed a theory which explains not only the presence of the unmodified line but also the width of the modified line. This theory takes into account both the motion and the binding energy of a scattering electron in its orbit and it gives a formula for the fraction of the total number of electrons which are in orbital positions such as to scatter modified x-rays in a direction ϕ. If we denote this fraction by $p(\phi)$ and use a subscript to denote the orbit which is occupied by the electrons considered, (for example $p_K(\phi)$ denotes the fraction of K electrons which are in a position to scatter modified x-rays in the direction ϕ then $p_K(\phi)$ is approximately given by

$$p_K(\phi) = \frac{\alpha_0 \text{ vers } \phi + 2\sqrt{2\alpha_s} \sin\frac{1}{2}\phi - \lambda_0/\lambda_s}{4\sqrt{2\alpha_s} \sin\frac{1}{2}\phi} \tag{3}$$

where $\alpha_s = h/mc\lambda_s$, $\alpha_0 = h/mc\lambda_0$, λ_s denotes the K critical absorption wave-length of the scattering substance, λ_0 the wave-length of the incident radiation and ϕ the direction of scattering. The values of $p_L(\phi)$, $p_M(\phi)$, etc., are obtained by means of similar formulas, when the orbits are circular and by more complicated formulas in the case of elliptic orbits.[5,7] $p(\phi)$ is now obtained as a weighted mean of the values for the various orbits. Jauncey and DeFoe[6] have shown that the theoretical value of s_2 is given by

$$s_2 = \frac{Kp(\phi)\{1 + \cos^2\phi + 2\alpha_0(1+\alpha_0) \text{ vers } \phi\}}{2(1+\alpha_0 \text{ vers } \phi)^5} \tag{4}$$

where K is given by

$$K = (NZ\rho/W)(e^4/m^2c^4) \; . \tag{5}$$

In Eq. (5) N denotes Avogadro's number, Z the number of electrons per molecule, ρ the density, W the molecular weight of the scattering substance, e the electronic charge, m the mass of an electron, and c

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[4] G. E. M. Jauncey, Phys. Rev. **25**, 314 (1925).
[5] G. E. M. Jauncey, Phys. Rev. **25**, 723 (1925).
[6] Jauncey and De Foe, Phil. Mag. **1**, 711 (1926).
[7] G. E. M. Jauncey, Phys. Rev. **27**, 687 (1926).

the velocity of light in vacuo. Jauncey and DeFoe[6] have pointed out that although s_2 should be given by Eq. (4) yet it is not a necessary result of the theory that s_1 should be given by replacing the factor $p(\phi)$ in the right side of Eq. (4) by $\{1-p(\phi)\}$. This could only be done if the probability of an electron's scattering in the direction ϕ were the same irrespective of whether the electron was in a position to scatter modified or unmodified rays. If the ratio s_1/s_2 can be measured experimentally, then Jauncey[7] has shown that the ratio of the probability P_U that an electron will scatter in a direction ϕ when in a position to scatter unmodified rays to the probability P_M that it will scatter modified rays is given by

$$P_U/P_M=(s_1/s_2)(p(\phi)/\{1-p(\phi)\} \tag{6}$$

The experiments of Barkla and Ayers,[8] Hewlett,[9] and Jauncey and May[10] show that there is scattering considerably in excess of the Thomson[11] value at $\phi=30°$ in the case of scattering by light elements. On Jauncey's theory however it is at 30° that the fraction $\{1-p(\phi)\}$ becomes considerable and therefore a considerable portion of the scattered rays are unmodified. Further, Barkla and Dunlop[12] find considerable excess scattering from heavy elements such as copper even when $\phi=90°$. Here again the fraction $\{1-p(\phi)\}$ becomes large when $\phi=90°$ when x-rays are scattered by copper. Again Hewlett[9] and Jauncey and May[10] find that when x-rays are scattered by light elements the scattering goes to zero at about $\phi=5°$. At this angle $p(\phi)$ vanishes. It seems then that excess scattering and also the zero scattering at small angles is a property of the unmodified scattering and not of the modified scattering. It is therefore evident that it is important to measure s_1 and s_2 experimentally, so that we may test the theoretical formula, Eq. (4), and also so that we may obtain s_1 as an empirical function of ϕ. As a preliminary attack on this problem the experimental values of $s_2/(s_1+s_2)$ have been determined for different scattering substances, different wave-lengths and for different angles of scattering.

2. THEORY OF THE EXPERIMENTAL METHOD

The experimental value of the scattering coefficient σ_{exp} determined by previous observers has always been approximately the sum of the two scattering coefficients σ_1 and σ_2. In the determination of σ_{exp} there is a slight error introduced by assuming the same absorption coefficient for the scattered as for the primary radiation, whereas in fact there is a slight increase in the absorption coefficient as shown experimentally by Sadler and Mesham.[13] This error is small but always tends to make σ_{exp} less than the true value. The softening is of course due to the change in wave-length of the modified portion of the scattered x-rays. This suggests that, since we know the change of wave-length on scattering and therefore also the change in absorption coefficient of the modified x-rays on scattering, we can separate s_1 and s_2 at a given value of ϕ by transferring a certain thickness of absorbing material from a position P in the primary beam to a position Q in the scattered beam and observing either the intensity of the scattered x-rays if the intensity of the primary x-rays is kept constant or the change in the intensity of the primary rays necessary to keep the intensity of the scattered x-rays constant. In the present experiment the second alternative was used. Jauncey and DeFoe[6,14] have given formulas for determining the ratio $s_2/(s_1+s_2)$ for two cases. First, for the case in which the scattering block is placed in a position such that a normal to its face makes an angle $\theta=\phi/2$ with the forward direction of the primary beam, ϕ being the scattering angle, we have

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[8] Barkla and Ayres, Phil. Mag. **21**, 275 (1912).

[9] C. W. Hewlett, Phys. Rev. **20**, 688 (1922).

[10] Jauncey and May, Phys. Rev. **23**, 128 (1924).

[11] J. J. Thomson, Conduction of Electricity through Gases 2nd Ed., p. 325.

[12] Barkla and Dunlop, Phil. Mag. **31**, 222 (1916).

$$s_2/(s_1+s_2)=\frac{y-1}{(y-1)+[(1-e^{-g})/ge^{-g}]e^{-(kd_1+b)}(1-ye^{-kd})}\,. \tag{7}$$

Second, for the case in which the scattering block is set in such a position that the plane of its face bisects the scattering angle ϕ, we have

$$s_2/(s_1+s_2)=\frac{y-1}{(y-1)+Be^{-kd_1}(1-ye^{-kd})}\,. \tag{8}$$

In the above equations the symbols used are defined as follows: $y=I_2/I_1$ where I_1 and I_2 are the intensities of the primary x-rays before and after the transfer of a thickness d of absorbing material from P to Q, the values of I_1 and I_2 being such that the intensity of the scattered rays is the same after the transfer as before; d_1 is the thickness of absorbing material at Q_1 which is not transferred (e. g. the thickness of the aluminum window of the ionization chamber); $k=(\mu_2-\mu_1)$; $b=(\mu_6-\mu_5)R+g$; $g=(\mu_4-\mu_3)t\sec\frac{1}{2}\phi$, where t is the thickness of the scattering block and ϕ is the angle of scattering; $B=$

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[13] Sadler and Mesham, Phil. Mag. **24,** 138 (1912).

[14] Jauncey and DeFoe, Proc. Nat. Acad. Sci. **11,** 517 (1925).

$e^{-hR}/\{1+(\mu_4-\mu_3)/2\mu_3\}$; $h=(\mu_6-\mu_5)$; R is the distance from scattering block to ionization chamber window ; μ_1 is the absorption coefficient of primary x-rays in absorbing material ; μ_2 is the absorption coefficient of modified x-rays in absorbing material ; μ_3 is the absorption coefficient of primary x-rays in scattering material ; μ_4 is the absorption coefficient of modified x-rays in scattering material ; μ_5 is the absorption coefficient of primary x-rays in air ; and μ_6 is the absorption coefficient of modified x-rays in air.

The change in absorption coefficient $k=(\mu_2-\mu_1)$ may be determined, either by plotting the experimental value of μ for the particular absorbing substance used against λ and reading from the curve the two values of μ corresponding to λ_ϕ and λ_0, or by making use of the relation

$$\mu/\rho = \text{const}\times\lambda^3+\sigma/\rho \tag{9}$$

In the present experiments aluminum was used for the absorbing material which was transferred from P to Q and Hewlett[15] gives the constant for aluminum in Eq. (9) as 12.4. If Eq. (9) is differentiated with respect to λ we obtain $\delta(\mu/\rho)$. Since σ/ρ varies slowly with the the wave-length we can treat it as a constant. We then have for aluminum

$$(\mu_2-\mu_1)=100.6\lambda_0^2(\lambda_\phi-\lambda_0), \tag{10}$$

$(\lambda_\phi-\lambda_0)$ being given by Eq. (1).

3. Experimental Arrangement and Procedure

The equations giving the ratio $s_2/(s_1+s_2)$ suggest the use of a balance method. The experimental arrangement is shown in Figs. 1 and 2. Two primary beams 1 and 2 which are in the same vertical plane are taken from the x-ray tube R which was placed at an angle of approximately 45° with the plane containing the two beams so as to eliminate any effect due to polarization in the primary rays. These were passed through the two slits C and D. C was about one square centimeter in area and its size was fixed. D could be varied from zero to about two square centimeters in area. The area of D was measured to .01 mm² by means of a micrometer screw. Absorbing material was placed at P_1 and P_2. Aluminum was used for absorbing material because the fluorescent radiation of aluminum does not interfere and because aluminum can be obtained commercially in a much higher state of purity than any other suitable substance. The scattered beams 1′ and 2′ from AB after passing through the absorbing material at Q_1 and Q_2 entered separate ionization chambers. These ionization chambers were connected by a glass tube and methyl iodide introduced by means of evaporation from a reservoir. This kept the concentration of methyl iodide vapor the same in the two chambers. The outer electrodes of the two ionization chambers were respectively connected to the opposite poles of a battery giving 180 volts, the middle point of the battery being grounded. The inner electrodes of the chambers were connected to each other and to a Compton electrometer. If the intensities of the scattered rays entering the two chambers is the same the electrometer shows no deflection. In these experiments the same thickness of aluminum was first placed at P_1 and P_2 also the thickness at Q_1 was the same as at Q_2. A balance was then obtained by varying the slit C by means of the micrometer screw and the reading of the micrometer recorded. Second, a certain thickness of aluminum d was then transferred from P_1 to Q_1. In order to restore the balance it was then necessary to open the slit C by a definite amount. After the balance had been restored, the micrometer was again read. These two readings were taken as proportional to the intensities I_1 and I_2 in Eqs. (7) and (8). It remained necessary to find the wave-length of the x-rays used. This was done by opening the slit C to double its value when the amount of aluminum at P_1 and P_2 was equal, (the aluminum which was transferred from P_1 to Q_1 was replaced prior to this determination) then sufficient additional aluminum was placed at P_1 to restore a balance. From this added thickness, the average wave-length of the primary beam was calculated.

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[15] C. W. Hewlett, Phys. Rev. **17**, 284 (1921).

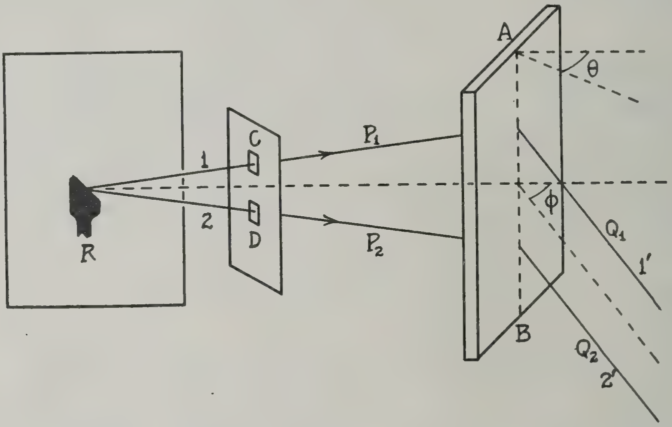

Fig. 1. Diagram of apparatus showing scattering block in the position of Method I, Eq. (7).

The electrometer used in determining the balance had a sensitivity of about 3000 to 5000 scale divisions per volt. All wires leading to the electrometer were insulated by means of quartz and were placed inside grounded conductors. In this way it was possible to avoid insulation leaks and electrostatic fluctuations. A further precaution was taken to avoid any steady change in conditions which might occur during a set of observations by taking readings in groups of five. For example, let I_1 denote the micrometer reading when the aluminum was at P_1 and I_2 the reading at Q_1, then consider a group of five readings, say three of I_1 and two of I_2, in which case the first, third and fifth were of I_1 and the second and fourth of I_2 or vice versa. The average values of I_1 and I_2 were then determined and a value for $y=I_2/I_1$ calculated. Three such groups of readings were made for each angle in the case of any given wave-length and substance. The values of y so obtained were then averaged and the ratio calculated from this average value. Even with these precautions the error in some cases is probably as much as ten percent. The carbon block used was .5 cm thick and was placed in the position of Method I, Eq. (7), Fig. 1. For aluminum the position was the same but the thickness was reduced to .166 cm. In the case of copper the block was placed in the position of Method II, Eq. (8), Fig. 2, and was thick enough to absorb all the x-rays. The distance R of the block from the ionization chamber window was always 13 cm.

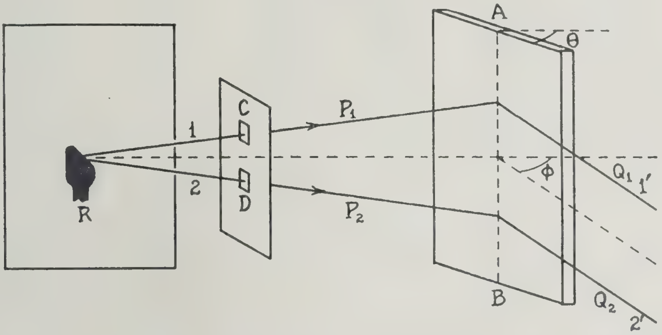

Fig. 2. Diagram of apparatus showing scattering block in the position of Method II, Eq. (8).

It should be mentioned that in the case of carbon it was necessary for the aluminum window of the ionization chamber to have a thickness of .045 cm in order to remove the characteristic rays of iron from the scattered beam. These characteristic rays were due to impurities in the carbon block. Calculations showed that a small percentage of iron as an impurity would entirely vitiate the results unless the window used was sufficiently thick to absorb all the characteristic radiation of iron. The thickness used was known to be sufficient since it was the same as that used for copper, and previous tests had shown that this thickness was sufficient to reduce the characteristic radiation of copper to a negligible amount.

4. RESULTS AND DISCUSSION

The experimental results for carbon, aluminum and copper are shown in Tables I, II, and III.

TABLE I

Carbon

ϕ	λ	y	d	d_1	$\frac{s_2}{s_1+s_2}$	$p(\phi)$	P_U/P_M
60	.345	1.047	.332	.045	.965	.977	1.1
60	.385	1.052	.322	.045	.857	.958	3.8
60	.435	1.052	.332	.045	.676	.920	5.5
60	.58	1.022	.083	.045	.623	.877	4.3
90	.325	1.087	.332	.045	.99	1.00	...
90	.475	1.192	.332	.045	.975	.980	1.3
90	.53	1.198	.332	.045	.82	.96	5.2
110	.31	1.109	.332	.045	1.00	1.00	...
110	.41	1.209	.332	.045	1.00	1.00	...
110	.45	1.222	.322	.045	.965	1.00	...
130	.33	1.157	.332	.045	1.00	1.00	...
130	.355	1.173	.322	.045	.975	1.00	...
130	.42	1.290	.332	.045	1.00	1.00	...

In these tables ϕ is the angle of scattering, λ the wave-length in angstroms, y the ratio I_2/I_1, d the thickness of the aluminum transferred. It is to be noted that the ratio $s_2/(s_1+s_2)$ is always less than $p(\phi)$ except where each is equal to unity. This means that the probability P_U of an electron's scattering unmodified rays in a direction ϕ is always greater than the probability P_M of an electron's scattering modified rays. In the last columns of the tables are shown the ratio

TABLE II

Aluminum

ϕ	λ	y	d	d_1	$\frac{s_2}{s_1+s_2}$	$p(\phi)$	P_U/P_M
90	.31	1.047	.332	.045	.67	.950	9.5
90	.36	1.065	.332	.045	.625	.939	9.0
90	.50	1.033	.083	.045	.537	.910	8.5
110	.30	1.079	.332	.045	.814	.965	6.1
110	.36	1.112	.332	.045	.783	.952	3.6
110	.50	1.051	.083	.045	.760	.920	5.0
130	.28	1.100	.332	.045	.926	.974	3.0
130	.33	1.134	.322	.045	.895	.964	3.1
130	.385	1.180	.332	.045	.865	.953	3.2

of these two probabilities. There are several blanks in the last column where the value of P_U/P_M is indeterminate. It might be mentioned that Woo[16] also finds $s_2/(s_1+s_2)$ to be less than $p(\phi)$ for Mo$K\alpha$ x-rays scattered from various elements.

TABLE III

Copper

ϕ	λ	y	d	d_1	$\frac{s_2}{s_1+s_2}$	$p(\phi)$	P_U/P_M
90	.27	1.035	.332	.045	.62	.90	5.5
90	.32	1.049	.332	.045	.609	.79	5.1
90	.36	1.059	.332	.045	.58	.67	5.2
100	.27	1.050	.332	.045	.74	.923	4.2
100	.32	1.071	.332	.045	.73	.901	3.3
100	.36	1.083	.332	.045	.68	.884	3.6
100	.41	1.096	.332	.045	.63	.849	3.3
130	.27	1.093	.332	.045	.94	.948	1.2
130	.345	1.144	.332	.045	.89	.916	1.4
130	.48	1.061	.083	.045	.81	.867	1.5

Jauncey[7] has shown that the unmodified scattering should disappear at an angle and a wave-length such that $p(\phi)$ becomes unity. This occurs at a value of ϕ given by

$$\text{vers}\,\phi=(3+2\sqrt{2})(\lambda_0^2/\lambda_s)(mc/h) \tag{11}$$

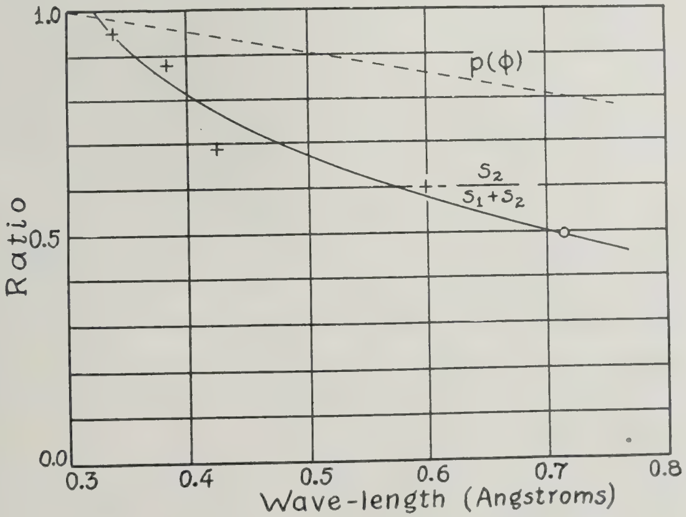

Fig. 3. Scattering from carbon at 60°.

A test of this formula has been made for scattering by carbon. The experimental values of $s_2/(s_1+s_2)$ are plotted against λ for the angles

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[16] Y. H, Woo, Phys. Rev. **27**, 119 (1926).

60° and 90° and are shown as the full curves in Figs. 3 and 4 respectively. It is seen that $s_2/(s_1+s_2)$ becomes unity at wave-lengths of 0.32A and 0.46A for angles of 60° and 90° respectively. For carbon the K absorption limit is 47A and solving Eq. (11) at values of $\phi=60°$ and 90° we obtain $\lambda_0=.31$A and .44A respectively. These agree very well with the experimental values. In the case of carbon at $\phi=110°$ the solution of Eq. (11) for λ_0 is 0.51A. As all the wave-lengths examined were less than 0.51A the ratio $s_2/(s_1+s_2)$ is approximately 100 percent. It will be noted that experimental values of $s_2/(s_1+s_2)$ are shown in Figs. 3, 4 and 5 for $\lambda=0.71$A. These values are taken from results obtained by Woo[16] for the scattering of MoK x-rays by carbon. It is seen that Woo's values fall upon the extrapolated portion of the curve as determined by the writer. The writer's values are therefore consistent with those of Woo. The broken curves in Figs. 3 and 4 are the graphs of $p(\phi)$ against λ for 60° and 90° respectively. It is seen that the curves for $s_2/(s_1+s_2)$ fall below the curves for $p(\phi)$ except where each becomes unity.

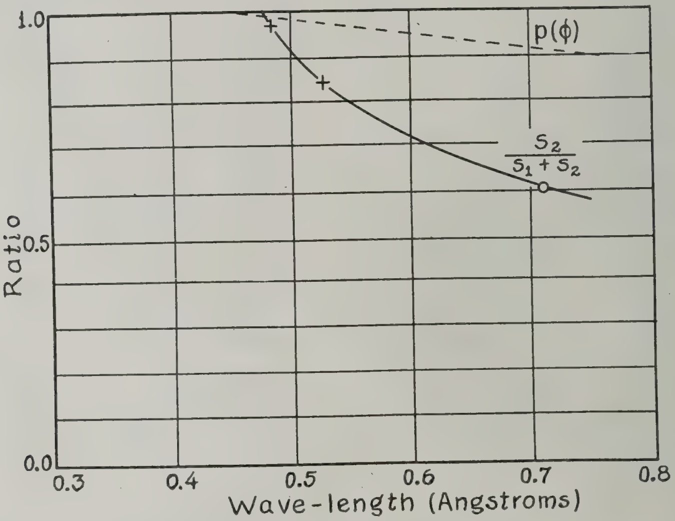

Fig. 4. Scattering from carbon at 90°.

The smooth curves of Figs. 5 and 6 are the graphs of $s_2/(s_1+s_2)$ against λ for aluminum and copper at $\phi=90°$. These curves are not extrapolated to cut the 100 percent line because the amount of the extrapolation would be so large that the results would be of little value. We may however use the results for copper to test the truth of Eq. (4). The experimental value of (s_1+s_2) has been determined for copper at 90° and a wave-length of .4A. Interpolating the results of Barkla and Dunlop[12] we find the value of (s_1+s_2) to be $1.40s_0$ where s_0 is the Thomson value at 90°. A similar determination by DeFoe and Jauncey[14] gives $(s_1+s_2)=1.24s_0$. The mean of these values is $1.32s_0$. The experimental value of $s_2/(s_1+s_2)$ for $\lambda=0.4$A at $\phi=90°$ is from Fig. 6 found to be 0.54. Hence $s_2=0.54\times1.32s_0=0.71s_0$.

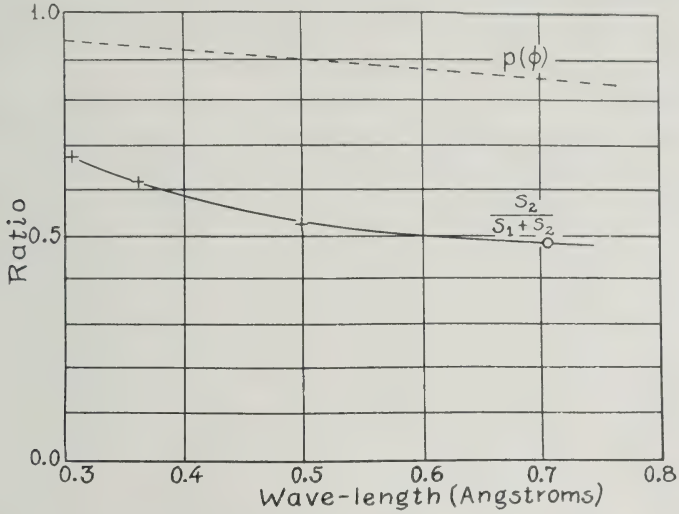

Fig. 5. Scattering from aluminum at 90°.

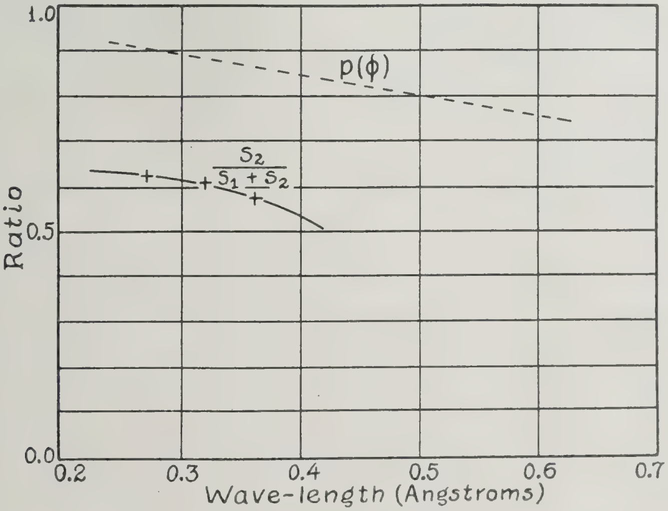

Fig. 6. Scattering from copper at 90°.

When unmodified rays are present the theoretical value of s_2 is given by Eq. (4). In the present case $p(\phi)$ has the numerical value of 0.85.

The value of the remainder of the right side of Eq. (4) is $0.87s_0$ for $\lambda=0.4$A. Hence $s_2=0.74s_0$ which agrees well with the experimental value $0.71s_0$. The use of s_1 is of course the difference between (s_1+s_2) and s_2 is therefore $0.58s_0$. It is unfortunate that more values of (s_1+s_2) are not available for various scattering substances, wave-lengths and angles of scattering for then we could arrive at a relation between s_1, λ and ϕ.

On examining the values of the ratio of P_U/P_M as given in the last columns of Tables I, II and III, we note a general tendency for the ratio for a given wave-length to become less as the angle increases. In fact in the case of copper the ratio seems to approach unity at an angle of about 130°. The results for carbon and aluminum are not quite so definite, but it must be remembered that the ratios, $s_2/(s_1+s_2)$, as given in the sixth column are not so accurate as could be desired and it might well be that the values of P_U/P_M even for carbon and aluminum approach unity for large angles. This approach to unity implies that the unmodified scattering per electron in a direction ϕ approaches the modified scattering per electron when ϕ becomes large.

The experimental results so far as they go support Jauncey's theory of the unmodified line in that the unmodified scattering disappears for a given angle at the wave-length demanded by the theory and also in that the experimental value of the modified scattering coefficient at 90° for copper is in agreement with the theoretical value.

In conclusion, the writer wishes to express his thanks to Professor G. E. M. Jauncey who suggested this problem, for his aid an interest in the carrying out of this research.

Washington University,
St. Louis, Mo.
March 2, 1926.

JUNE, 1926 PHYSICAL REVIEW VOLUME 27

NOTE ON THE QUANTUM THEORY OF THE UNMODIFIED LINE IN THE COMPTON EFFECT

By G. E. M. Jauncey

Abstract

Disappearance of the unmodified line.—According to the theory developed in two previous papers (Phys. Rev. 25, 314 and 723) it is shown that the unmodified line should disappear at a scattering angle ϕ given by vers $\phi = (3+2\sqrt{2})(\lambda_0^2/\lambda_s)(mc/h)$ where λ_0 is the wave-length of the primary x-rays and λ_s the K critical absorption wave-length of the scattering substance. This formula shows that there is an unmodified line for all values of ϕ when Mo Kα rays are scattered by carbon and heavier elements, but when scattered by boron and lithium this line should disappear at 147° and 60° respectively. *Ratio of the energies in the modified and unmodified lines.*—The theory of the previous papers gives the ratio of the number of electrons in orbital positions U such as to scatter unmodified rays in a direction ϕ to the number of electrons in orbital positions M such as to scatter modified rays. A formula for the ratio of the probability of an electron scattering when in the U position to that when in the M position is given together with a simpler method for calculating the number of electrons in the M position to the number in the U and M positions for elliptic orbits.

1. Disappearance of the Unmodified Line

In two previous papers,[1,2] the writer has explained the existence of the unmodified line in the Compton effect by showing that there is a certain range of positions of the scattering electron of a given type (K, L, etc.) in its Bohr orbit from which the electron cannot be ejected from the atom by the scattering process when x-rays are scattered at an angle ϕ with the direction of the primary rays. For convenience, we shall speak of an electron which is in an orbital position such that it cannot be ejected by the scattering process as being in the U position and of an electron which is in a position such that it can be ejected as being in the M position. Jauncey's theory requires that for scattering in a direction ϕ by a given type of electrons the ratio of the number N_M of electrons in the M position to the total number (N_U+N_M) of electrons in the U and N positions is approximately given by

$$\frac{N_M}{N_U+N_M}=\frac{\alpha_0 \operatorname{vers}\phi+2\sqrt{2\alpha_s}\sin\frac{1}{2}\phi-\lambda_0/\lambda_s}{4\sqrt{2\alpha_s}\sin\frac{1}{2}\phi}, \tag{1}$$

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[1] G. E. M. Jauncey, Phys. Rev. **25,** 314 (1925).

[2] G. E. M. Jauncey, Phys. Rev. **25,** 723 (1925).

where λ_0 is the wave-length of the primary x-rays, λ_s is the critical absorption wave-length for the particular type of electrons under consideration, $\alpha_0 = h/mc\lambda_0$ and $\alpha_s = h/mc\lambda_s$. Eq. (1) is true for those types of electrons which move in circular orbits, while a more complicated formula[2] exists for electrons which move in elliptic orbits.

The ratio $N_M/(N_U+N_M)$ is to be taken as zero when the right side of Eq. (1) is negative and as unity when the right side is greater than unity. For values of the right side between zero and unity, the ratio increases as ϕ increases and as λ_s decreases. The ratio is therefore least for the K electrons. Hence when the ratio becomes unity for the K electrons, it will be unity for all the other electrons, and we shall have no unmodified line. Therefore, equating the right side of Eq. (1) to unity and solving for ϕ, we obtain the value of ϕ for which the unmodified line in the Compton effect should disappear. This value of ϕ is given by

$$\text{vers}\,\phi = (3+2\sqrt{2})(\lambda_0^2/\lambda_s)(mc/h) \tag{2}$$

If λ_0 and λ_s are measured in angstroms, Eq. (2) may be written vers $\phi = 242(\lambda_0^2/\lambda_s)$. For the scattering of MoKα x-rays by the K electrons of carbon we have $\lambda_0 = 0.71$A and $\lambda_s = 47$A, so that the right side of Eq. (2) is greater than 2 and there is no real solution for ϕ. A similar result holds for the scattering of MoKβ x-rays by carbon. Hence there is an unmodified line for all values of ϕ when MoKα and MoKβ x-rays are scattered by carbon and elements of higher atomic number than carbon. However, for the K electrons of boron we have $\lambda_s = 66$A and there is now a real solution for ϕ. For scattering by boron the unmodified line should disappear at $\phi = 147°$, while the unmodified Kβ line should disappear at $\phi = 117°$.

Jauncey, Boyd and Nipper[3] have tested this experimentally by scattering MoK x-rays by boron at about 145° to 150°, the scattered spectrum being examined photographically by means of a Sieman-Ross x-ray spectrometer. The photograph showed the modified Kα and Kβ lines plainly but the unmodified lines were not apparent although in a comparison experiment where carbon was the scattering substance the unmodified lines were evident. As further experimental evidence Allison and Duane[4] and Woo[5] have scattered MoK x-rays from lithium at angles greater than 60° and find either very little or no evidence of the unmodified lines. For the K electrons of lithium $\lambda_s = 240$A, so that the unmodified MoKα and Kβ lines should disappear at 60° and 53° respectively. It might be mentioned that the existence of the unmodified MoKα line might have been explained on the following assumptions: (1) the electrons are at rest in the atom, (2) the energy given to the electron by the scattering process is that given to a free electron, and (3) there is an unmodified line unless this energy is greater than the binding energy of the electrons. These assumptions give the condition vers $\phi=(\lambda_0^2/\lambda_s)(mc/h)$ for the disappearance of the unmodified line, which in the case of carbon should be at 75°. Experimentally, however, the unmodified MoKα line does not disappear at any angle when the x-rays are scattered from carbon. We are therefore left with the theory of the unmodified line as developed by Jauncey[1] as being the only available explanation.

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[3] Jauncey, Boyd and Nipper, Phys. Rev. **27,** 103 (1926).

[4] Allison and Duane, Phys. Rev. **26,** 300 (1925).

[5] Y. H. Woo, Phys. Rev. **27,** 119 (1926).

2. RATIO OF THE ENERGIES IN THE MODIFIED AND UNMODIFIED LINES

Jauncey and DeFoe[6] have shown that the assumption that the chance P_U that an electron will scatter in the direction ϕ when in the U position is equal to the chance P_M that an electron will scatter when in the M position is not necessary to Jauncey's theory of the unmodified line. Experiments show that P_U is greater than P_M and we are able to calculate the ratio P_U/P_M from experimental data. Eq. (1) gives the ratio $N_M/(N_U+N_M)$ for a given type (K, L etc.) of scattering electrons so long as these electrons are moving in circular orbits. If, however, the electrons are moving in elliptic orbits the method of calculation is as follows: Referring to Fig. 1 the curves $ABCD$ and $DEFG$ are taken from Fig. 3 in Jauncey's paper.[2] The curve $ABCD$ is for circular orbits while the curve $DEFG$ is representative of the curves for elliptic orbits. If the line AD is divided at L in the ratio LD/AD such that this ratio is given by the right side of Eq. (1) and the line LM is drawn perpendicular to AD then the ratio $N_M/(N_U+N_M)$ for the particular type of electrons under consideration is given by the ratio of the area $LMFGK$ to the area $HDEFGK$. The weighted mean of the ratios $N_M/(N_U+N_M)$ for the various types of electrons is represented by $p(\phi)$. If now s_1 and s_2 represent the unmodified and modified scattering coefficients per unit solid angle in the direction ϕ, then the ratio s_2/s_1 can be found experimentally by the methods of Woo[5] and DeFoe.[7] We then have

$$P_U/P_M=(s_1/s_2)\cdot p(\phi)/\{1-p(\phi)\} \tag{3}$$

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[6] Jauncey and DeFoe, Phil. Mag. **1,** 711 (1926).

[7] O. K. DeFoe, Phys. Rev. **27,** 675 (1926).

Woo in a recent paper[5] finds the ratio s_2/s_1 by obtaining the spectrum of scattered MoKα x-rays and comparing the areas under the modified and unmodified humps in his curves. Woo finds s_2/s_1 for carbon at 90° to be 1.45. However Woo compares this with a value 1.74 for the ratio of the 'intensities' calculated on theoretical grounds in a paper by the writer.[2] In this paper[2] the writer distinguishes between 'intensity' and 'energy.' In the sense in which the writer has used the words, Woo has measured the ratio of the 'energies.' The writer has used the word 'intensity' to denote the height of the ordinate of the most intense part of the modified or unmodified hump and not the area under the hump; while the word 'energy' implies the area. According to the argument of the paper[2] the ratio of the 'energies' for MoKα x-rays scattered at 90° by carbon is 10.9 and by sulfur is 4.2. These values, however, are based on the assumption that $P_U = P_M$. As s_2/s_1 is quite evidently smaller than the ratio of the 'energies,' we see that P_U is greater than P_M and from Eq. (3) the ratio P_U/P_M for MoKα x-rays scattered by carbon at 90° is $10.9/1.45 = 7.5$. Thus we see that scattering is about 7.5 times as probable when the electron is in the U position as in the M position. It should be remarked that Eq. (3) gives only the mean value of P_U/P_M. It might well be that this ratio has different values for the different orbits.

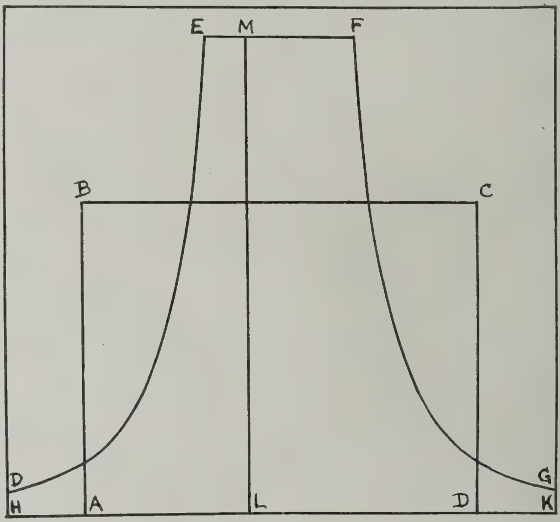

Fig. 1. Curves for obtaining the ratio $N_M/(N_U+N_M)$ for elliptic orbits.

Washington University,
St. Louis, Mo.
March 3, 1926.

JUNE, 1926 PHYSICAL REVIEW VOLUME 27

THE REFRACTION OF X-RAYS IN PRISMS OF VARIOUS MATERIALS

By C. M. Slack

Abstract

The method consisted in the use of the "double x-ray spectrometer" for measuring the extremely small changes in angle produced by refraction in prisms, which were placed between two crystals. The rocking curves from the second crystal were from 6 to 10 seconds of arc wide at half maximum and, under favorable temperature conditions, a shift of .2 seconds could be detected. Two different wave-lengths of x-rays and prisms of various materials were used. The values of $\delta\times10^6$, where $\delta=1-\mu$, are as follows:

λ	silver	copper	sulfur	aluminum	carbon	celluloid	paraffin
.7078A	5.85±.3	5.95±.5	1.39±.05	1.68±.07	1.23±.15	.980±.03	.701±.03
1.537 A				8.40±.2		4.78 ±.1	3.28 ±.15

These results agree with the Lorentz dispersion formula within experimental error. In the case of certain materials, notably graphite, the curves from the second crystal were extremely broad (20 to 50 seconds), caused by internal refraction due to the granular structure. This seems of interest with respect to the possibility of comparing internal arrangements of particles in various samples, though nothing of that sort was attempted here.

Introduction

In a recent paper by Bergen Davis and C. M. Slack[1] a method was described which employed the "double x-ray spectrometer"[2] for the measurement of the refraction of x-radiation in an aluminum prism. The present paper presents a continuation of that work using a variety of substances as prisms.

Experimental Method

In all cases, except copper, silver and carbon, *double* prisms were used, in which the ray passed through the prism symmetrically, being bent the same at each surface. With copper and silver the difficulty experienced in perfecting the prism edge was overcome by backing a carefully polished face of the material against a steel plate and then milling the other face to the angle desired. The ray was then allowed to enter normally, refraction taking place on emergence. In these metals, on account of the high absorption, it was not possible to work at a distance greater than .01 cm from the edge. With carbon a right angled block was used, this being rotated to obtain the refracting angle.

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[1] Bergen Davis and C. M. Slack, Phys. Rev. **27,** 18 (Jan., 1926).

[2] Bergen Davis and W. M. Stempel, Phys. Rev. **17,** 608 (May, 1921).

In measuring the refraction, the first crystal was set for the wavelength desired (MoKα or CuKα) and a direct rocking curve from the second crystal was taken. Then the prism was inserted and the rocking curve again taken. The shift in the peak measured the bending of the ray in the prism. This process was usually repeated several times at different prism positions to make sure that the prism was across the x-ray beam and to iron out slight irregularities in the prism surfaces and the larger shifts due to temperature changes.

In calculating δ from the prism angle and the measured bending a simple modification of the formula for the refractive index of a material for light was used:

$$\delta = -\theta \cot R \tag{1}$$

for single prism:

$$\delta = -\tfrac{1}{2}\,\theta \cot \tfrac{1}{2} R \tag{2}$$

for double prism. R is the prism angle and θ the deviation of the ray. The sign of θ is negative for bending as observed, which gives a positive value for δ in every case.

RESULTS AND DISCUSSION

The results are shown in Table I.

TABLE I

Data on refraction of x-rays. Values of δ $(=1-\mu)$.

Substance	prism angle (degrees)		refraction (sec. of arc)	$\delta\times10^6$ observed	$\delta\times10^6$ Calc. by Lorentz formula	
					complete	omitting char. freq.
			.7078A			
silver	single	63.5	2.42±0.1	5.85 ±0.3	5.80	6.33
copper	single	60.0	2.12±0.2	5.95 ±0.5	5.72	5.60
sulfur	double	168.3	5.39±0.2	1.39 ±0.05	1.37	1.37
aluminum	double	166.0	5.62±0.2	1.68 ±0.07	1.77	1.77
carbon	single	86.4	4.02±0.5	1.23 ±0.15	1.10	1.10
celluloid	double	171.0	5.12±0.1	.980±0.03	.991	.991
paraffin	double	173.0	4.71±0.15	.701±0.03	.714	.714
			$\lambda=1.537$A			
aluminum	double	116.0	5.53±0.1	8.40 ±0.2	8.46	8.44
celluloid	double	144.0	6.06±0.1	4.78 ±0.1	4.71	4.71
paraffin	double	152.0	5.40±0.15	3.28 ±0.15	3.37	3.37

The first of the last two columns was obtained from a modification of the Lorentz dispersion formula[3] thus:

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[3] R. von Nardroff, Phys. Rev. **24,** 143 (1924).

$$\delta=\frac{e^2}{2\pi m}\left[\frac{n_1}{\nu^2-\nu_c{}^2}+\frac{n_2}{\nu^2}\right] \tag{3}$$

where ν_c is the critical absorption frequency for the K series.

Which for the last column was simplified to

$$\delta=\frac{e^2}{2\pi m}\;\frac{n}{\nu^2} \tag{4}$$

It will be observed that only in the cases of silver and copper did the consideration of ν_c have an appreciable effect and in these it brought the result nearer the experimental value.

The curves were extremely narrow and of almost perfect regularity. It seems of interest to note that, with the exception of a few cases mentioned below, the transmission curve had practically the same width as the direct. The peak of an individual curve could be located to within .2 seconds. A shift due to temperature caused considerable trouble, but as it affected both curves alike it could be largely eliminated by a series of "out" and "in" curves. The other errors, such as lining up of the prism in mounting, measuring of prism angle, imperfections in prisms, etc., were not so easy to determine but in no case would introduce an error greater than .2 seconds, and in most cases considerably less. The discrepancy in the case of carbon is due to curve broadening discussed below.

Fig. 1 is a direct curve which shows the accuracy with which the peak can be located under favorable conditions. It also shows to a fine degree the perfect structure of the crystals used.

Because of the relatively low absorption in celluloid and the high accuracy with which it was possible to mill the prism edge, quite large refractions could be obtained. Fig. 2 shows such a case. The prism was pushed only part way across the beam, (a) representing that which passed the edge and (b) the portion which was refracted in the prism.

INTERNAL REFRACTION IN GRAPHITE

In the determination of δ for carbon a piece of brush graphite kindly supplied by Dr. Welsh of the Union Carbide and Carbon Research Laboratories was used. It was observed immediately that the curves, instead of being 6 seconds wide at the half maximum, were of the order of 30 to 50 seconds, depending on the prism position. This effect apparently came from internal refraction due to the granular structure of the material. To check this, however, the transmission through a paraffin block was compared with that through the same amount granulated and it was found that the curve width was nearly doubled for the granulated material. There was some broadening in the case of sulfur, due to the same cause. In no case was the effect noticed where it could be attributed to the surface conditions though in every case surface irregularities were enormous as compared to the x-ray wavelength.

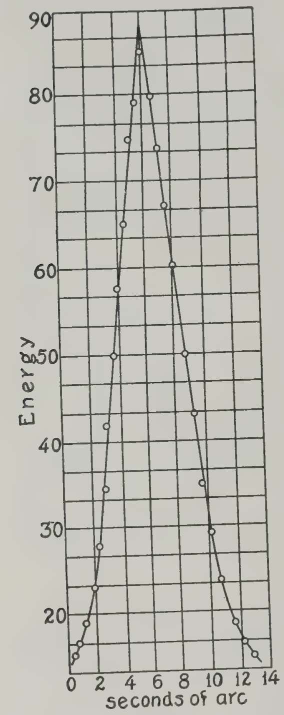


Fig. 1. Apparatus curve.

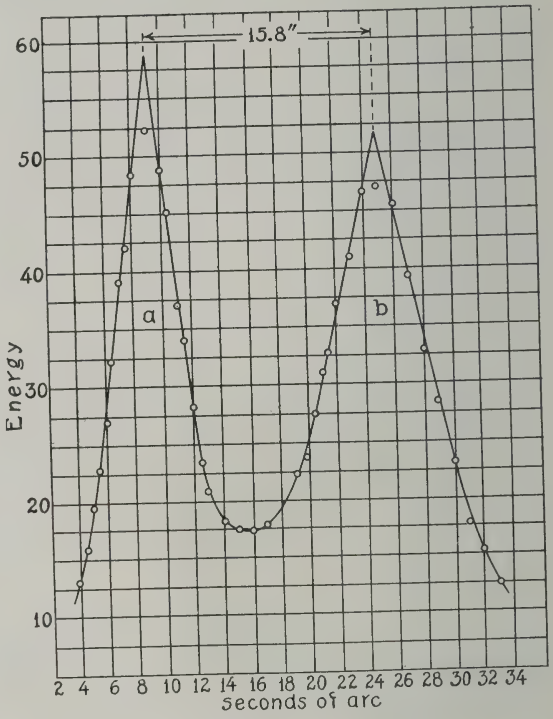


Fig. 2. Refraction in celluloid.

An investigation was made of the transmission through graphite strips of different thickness and the results obtained are given in Table II.

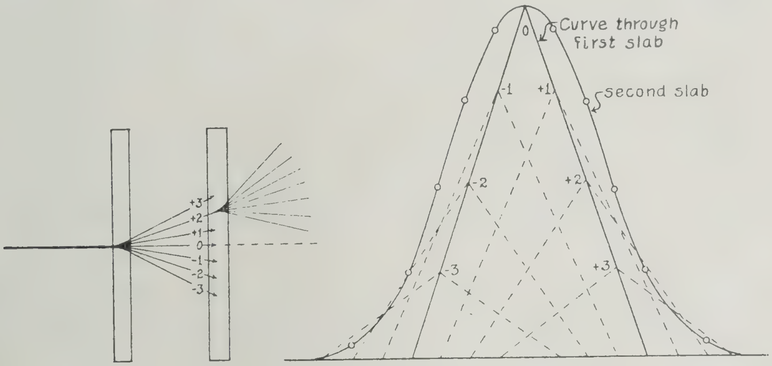
TABLE II

Data on the broadening of refraction curves in graphite.

Thickness of graphite	Curve width at half max.	Broadening	
	MoKα		
13.8 mm	58 sec.	52 sec.	±5
8.4	46	40	±5
4.3	30	24	±3
2.2	19	13	±3
1.2	15	9	±2
.62	10	4	±2
0.	6	0	...
	CuKα		
1.2	58	47	±5
.62	45	34	±4
0.	10.8	0	...

This variation of the broadening with thickness may be explained as follows. Consider the original beam as plane parallel and that in traversing a slab of known thickness it is divided into a large number of smaller elements (see Fig. 3) angularly dispersed in a manner which can be determined from a corresponding rocking curve. On traversing a second slab of equal thickness each of these small elements will be angularly dispersed in a manner exactly as was the original beam through the first slab. The total effect is then to be obtained by summation over all the elements.

The numerical value of the intensity at any angle is obtained experimentally as the height of that particular ordinate on the rocking curve. Thus to obtain the broadening graphically, curves were drawn, having the same distribution as the original, from a number of points on the original. Then the ordinates of the elementary curves were added and the scale reduced for comparison. (See Fig. 4). This gave a curve showing distribution of intensity after traversing a second unit slab. This process was repeated for each thickness. In practice some eight points were taken on each curve and the check with the experimental results was within the error of observation. To explain quantitatively the original broadening would demand a knowledge of the shape, size and distribution of the carbon particles, which is not available.



Figs. 3 and 4. Diagrams to illustrate how the internal refraction of x-rays in graphite broadens the rocking curves.

In conclusion I wish to express my appreciation to the members of the Physics Department for their cooperation in this work, and especially to Professor Davis for the suggestion of the problem and his constant aid in overcoming difficulties encountered.

Phoenix Physical Laboratories,
Columbia University,
January 7, 1926.

THE ORIGIN OF K-RADIATION FROM THE TARGET OF AN X-RAY TUBE

By Mark Balderston

Abstract

The fluorescent energy transformation coefficient, the ratio of the energy of secondary K-radiation emitted by an elementary volume of the radiator to the energy absorbed by it from the exciting x-rays, is observed for Fe, Ni, Cu, Zn, Mo, and Ag. The ratio of quanta emitted as K-radiation to quanta absorbed seems to be a constant for a given metal; Fe—33 percent; Ni—39 percent; Cu—43.5 percent; Zn—50 percent; Mo—83 percent; Ag—75 percent. Making use of the experimentally determined values of the transformation coefficient the *fluorescent K-characteristic radiation* from the target of an x-ray tube is calculated for Cu and Ag, and compared with observed values of the total K-radiation. An estimate is also made from theoretical considerations of the relative amounts of direct impact K-characteristic radiation to be expected from an x-ray tube target. The calculations indicate that for silver and probably for other elements of high atomic number practically all of of the K-characteristic radiation from an x-ray tube is fluorescent in origin while for copper and probably other elements of low atomic number a considerable part of the K-radiation is due to direct impact of the cathode electrons.

FOLLOWING the discovery by Kaye[1] that characteristic x-radiation was emitted by the target of an x-ray tube Barkla[2] explained the phenomenon as secondary radiation resulting from the absorption, in the target itself, of the general radiation. Beatty[3] examined the subject theoretically, not however publishing his method of analysis, and announced that not over ten per cent of the observed characteristic radiation could be so accounted for. An experimental investigation conducted with as much care as was possible with the facilities then available (1912) convinced him that practically all of the K-radiation from an x-ray tube target was the result of direct impact of the cathode electrons without the intermediate formation and absorption of general x-radiation.

With the x-radiation spectrometer came new evidence for Barkla's theory in the form of a sharp discontinuity in the general radiation spectrum at what was soon recognized as the K-absorption limit. Apparently the wave-lengths below the K-limit were strongly absorbed in the target and it was but natural to assume that the K-radiation was an indirect effect resulting from this absorbed energy. Under the influence of Beatty's work, however, this evidence was largely discounted and explained as due to absorption by small bumps on the face of the target. It seems to have been generally assumed that if the target were absolutely smooth there would be no such discontinuity; that the characteristic radiation would appear as a new effect superposed on the general radiation. Beatty's[3] investigation of the total radiation from a copper target added weight to these conclusions; for as the velocity of the impinging electrons was increased the intensity of the resulting x-rays increased being nearly proportional to the fourth power of the velocity until the K-radiation appeared when the rate of increase became more rapid as though a new effect were superposed on the old. A similar piece of work by Brainin[4] confirmed Beatty's result for copper and secured similar results for cobalt, palladium and platinum. Molybdenum, however, gave a perfectly straight line showing no break at the K-absorption limit while silver showed a well defined decrease in efficiency at about the voltage corresponding to the K-absorption limit.

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[1] G. W. C. Kaye, Phil. Trans. A**209,** 123–151 (1909).

[2] C. G. Barkla and C. A. Sadler, Phil. Mag. **17,** 739–760 (1909).

[3] R. T. Beatty, Proc. Roy. Soc. **87,** 511–518 (1912).

Meanwhile D. L. Webster and A. E. Hennings[5] have shown that for a molybdenum target, the focal spot of which had been fused so that there could not possibly be inequalities great enough to explain any discontinuity in the general radiation curve, nevertheless a well defined discontinuity appeared which they explained as wholly due to K-absorption in the target and from the amount of the discontinuity calculated the mean depth of production of the x-rays at the K-absorption limit. Their result is well in accord with the data on penetration of electrons found by Terrill.[6]

These results make it seem worth while to redetermine on the basis of present knowledge the amount of fluorescent or indirect K-radiation to be expected from the target of an x-ray tube. Our knowledge of absorption coefficients is adequate. The results of Terrill's work on electron penetration in metals gives at least a rough indication of the mean depth of production of general x-radiation of a given wave-length. Webster and Hennings' work mentioned above indicates its reliability. There remains to find what we have termed the "fluorescent transformation coefficient," ϕ, for a given range of wave-length of incident x-rays; i. e., the ratio of the energy of fluorescent

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[4] C. I. Brainin, Phys. Rev. **10,** 461 (1917).

[5] D. L. Webster and A. E. Hennings, Phys. Rev. **21,** 301–311 (1923).

[6] H. M. Terrill, Phys. Rev. **22,** 101–108 (1923).

K-radiation from a small element of the target to the total energy absorbed by the element during the same time. The determination of this coefficient for a number of metals ranging from iron (26) to silver (47) and for a number of wave-lengths from .314Å to .9Å was the object of the investigation of which this paper is a report.

Apparatus and Experimental Method

The apparatus is an x-ray spectrometer with calcite crystal *C* (Fig. 1) and a 15 cm ionization chamber *A*, containing air saturated with ethyl bromide vapor. The chamber is mounted so that it may be revolved about a vertical axis 2 cm in front of the aluminum window making it possible to use the same chamber for measuring the secondary radiation from the specimen *R* and when turned through an angle of 90° to position *B*, the exciting radiation (*R* being then removed). The face of the radiator *R* makes an angle of 45° with the incident

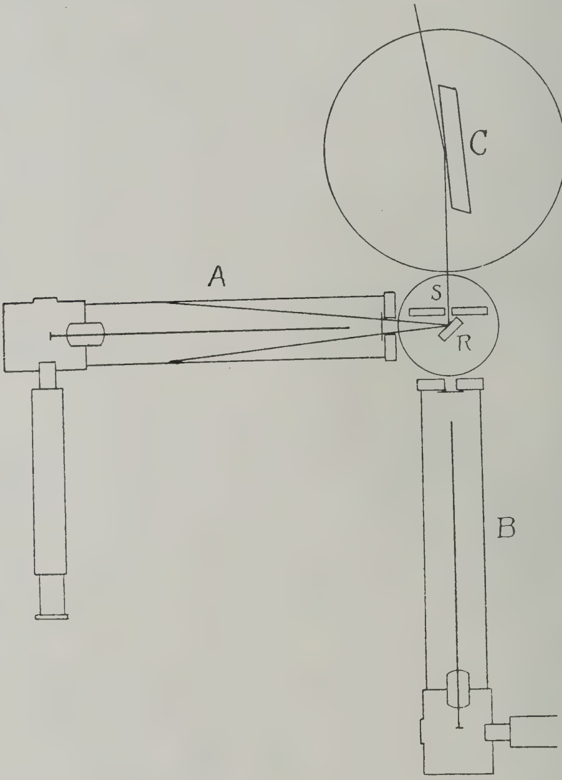

Fig. 1. Apparatus. *C* represents the calcite crystal, *A* and *B* the two positions of the movable ionization chamber, *R* the radiator, *S* the slit.

beam so that the path of the incident x-rays in the radiator is equal to the mean path of the resulting characteristic radiation which reaches the ionization chamber. (On account of the very large solid angle subtended by the window this condition is only approximately satisfied.) The ionization current is measured by the rate of collapse of a small gold leaf electroscope mounted on the end of the chamber. The insulated electrode and the gold leaf are charged to a potential of about 60 volts. The sensitivity of the electroscope is about five divisions per volt and as the capacity is small the sensitivity per unit charge is high. The source of x-rays is a water-cooled tungsten-target tube of the Coolidge type. This tube was kindly constructed for the Laboratories by the Research Department of the Westinghouse Lamp Company. The source of power was a 500 cycle voltage rectified by two kenotrons and smoothed out by a large condenser.

The tube voltage and current were adjusted to suitable values. The crystal table was set at the proper angle to reflect the wave-length desired and, with the ionization chamber in position *B* (see Fig. 1) the proper position of the slit *S* was determined. The ionization current was then taken several times in this position giving a good mean value as a measure of the incident or exciting radiation. The chamber was then turned to position *A* at right angles to position *B*. With the tube input maintained at the same value there were then taken in turn; first, the natural leak of the electroscope and chamber; second, the ionization current with the required radiator *R*, placed in position; third, the natural leak again (the radiator *R* having been removed). This was repeated many times during a run, using different radiators. Occasionally during a run the incident radiation measurement was repeated as there was usually a slight drift in sensitivity due to change in temperature. The leak varied capriciously. Not over ten percent of it was due to stray x-rays (except at the highest voltages used) as was readily determined by shutting off the power. The amount of the leak varied a great deal with the weather but the range of variation during a given run was no greater in summer than in late winter. It was found necessary to keep the electroscope system charged throughout a run. If it were allowed to become completely discharged, for even a few seconds, it would give abnormally high values for a considerable period, the effect disappearing logarithmically with the time. Extreme precautions were taken to return the ionization chamber to exactly the original position after a reading of the incident radiation.

The ratio of the ionization current due to the secondary radiation (corrected for leak) to the ionization current due to the incident radiation is given in Table I.

TABLE I

Ratio of the ionization currents due to secondary and incident radiations.

Incident Wave-length	Value of c'/c for Ag	Mo	Zn	Cu	Ni	Fe
.306Å	.0093	.0058	......	.00015	......	......
.359	.00826	.00653	.00065	.00052	......	......
.466	.00736	.00637	.00115	.00109	.00067	.00057
.571	......	.0065	.00127	.00119	.00096	.00063
.678	......	......	.00195	.00171	.00138	.00094
.782	......	......	.00233	.00204	.00158	.00125
.887	......	......	.00297	.00256	.00230	.00161

ENERGY TRANSFORMATION COEFFICIENT, ϕ

In order to compare the vaues of the transformation coefficients of molybdenum and silver with those of the lighter elements, the radiations from which do not excite the K-radiation in bromine of the ethyl bromide, it is necessary to reduce the ratio of ionization currents given in Table I to the ratio which would have been obtained if the radiation could have been completely absorbed in air. This was done by making use of Barkla's[7] data on relative ionization in air and ethyl bromide. On account of the difference in path in the ionization chamber of different pencils of the divergent beam of K-radiation it was necessary to integrate over the solid angle ω to get the correction factor A′ for the K-radiation. The energy transformation coefficient ϕ, the fraction of energy absorbed by a small elementary volume of the radiator which is re-emitted as K-radiation is given by the following expression

$$\phi = \frac{4\pi}{\omega}\left[M\int_0^{t\sec\pi/4} \mu e^{-\mu x} e^{-\mu_k a x} d\,x\right]^{-1} A'c'/Ac\,.$$

The integral accounts for absorption in the radiator of the exciting radiation before transformation and for absorption of the resulting K-radiation before emergence from the radiator. ω is the solid angle subtended at the radiator by the window of the ionization chamber. μ is the coefficient of absorption of the radiator for the exciting radiation. μ_K is the coefficient of absorption of the radiator for its own K-radiation. $A'c'$ is the total energy per second of K-radiation entering the ionization chamber, expressed in terms of the total ionization it can produce in air. Ac is the energy per second of the exciting radiation falling on the radiator, expressed in the same terms. M is a correction factor for absorption of the K-radiation in air and in the aluminum window of the ionization chamber. t is the thickness of the radiator. x is the path in the radiator of the exciting radiation before transformation. ax is the path in the radiator of the resulting K-radiation before emergence.

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[7] C. G. Barkla, Phil. Mag. **20**, 372 (1910).

The ratio c'/c is given in Table I. The value of ω is $.030\pm.004$. This is probably by far the least accurate factor entering into the determination of ϕ. The values of μ are from data of Richtmyer[8] and Hewlett.[9] Those of μ_K are from tables compiled by Ledoux-Lebard and Dauvillier.[10]

The amount of scattered radiation from the radiator entering the ionization chamber in position A is negligible. This is because of the fact that the coefficient of scattering is least at this angle (90°)[11] and that the shortness of the ionization chamber makes it relatively much more sensitive to the K-radiation than to the scattered radiations at the short wave-lengths. (It is only at short wave-lengths that the scattered radiation becomes important.)

The experimental values of ϕ are given in Table II below.

TABLE II

Values of ϕ, the ratio between the energy re-emitted as K-radiation by an elementary portion of the radiator to the energy absorbed by that portion from the incident or exciting x-radiation; and the values of the quantum transformation coefficient, u.

Wave-length of incident x-radiation			Values of ϕ for			
	Ag	Mo	Zn	Cu[12]	Ni	Fe
.306Å	.398	.264	....	.021	....	....
.359	.414	.323	.077	.066	....	....
.466	.611	.488	.160	.156	.090	.086
.571	....	.632	.166	.163	.121.	.089
.678	....	....	.220	.193	.142	.103
.782	....	....	.251	.218	.153	.124
.887	....	....	.311	.263	.210	.148
Values of u	.75	.83	.50	.435	.39	.33

THE QUANTUM TRANSFORMATION COEFFICIENT, u

If now we plot ϕ versus λ, the wave-length of the incident x-radiation we find the relationship is apparently linear and the curves cut the horizontal axis at points in the neighborhood of the origin. This suggests the possibility that the ratio of the number of quanta transformed to the total number of quanta absorbed is the same for a given radiator at all frequencies and that the decrease in ϕ with increase in frequency of the absorbed radiation is due to the increase, with frequency, in the energy of the absorbed quantum while the energy of the re-emitted quantum remains unchanged. The failure of the curves to pass through the origin may then be ascribed to lack of perfect proportionality between the calculated ionization and the energy of the radiation. If, now, the line be extended to the wave-length of the K-characteristic radiation it will represent an imaginary condition in which the absorbed quantum is equal to the re-emitted quantum and in consequence the ratio of the energy absorbed to the energy emitted will be equal to the ratio of the quanta absorbed to the quanta emitted. This quantity, u, has been derived from each of the curves in Fig. 2 and the values are shown in the last column of Table II.

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[8] F. K. Richtmyer, Phys. Rev. **18,** 13 (1921).

[9] C. W. Hewlett, Phys. Rev. **17,** 292 (1920).

[10] R. Ledoux-Lebard et A. Dauvillier, La Physique des Rayons X. Paris (1921).

[11] Barkla and Ayers, Phil. Mag. **21,** 270–278.

[12] At .385A G. E. M. Jauncey and O. K. DeFoe have found by a different method a single value of ϕ (for Cu) = .20 Proc. Natl. Acad. Sci. **11,** 520–2 (1925).

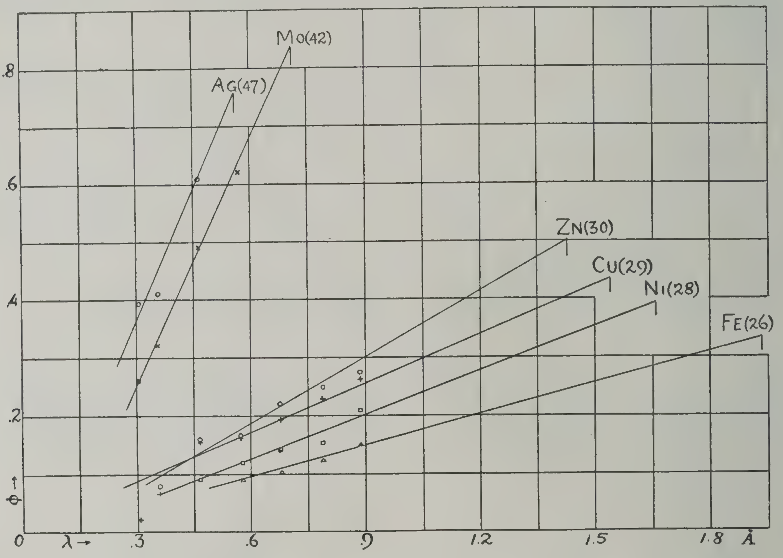

Fig. 2. Relation between ϕ and the wave-length of general x-radiation absorbed by the specimen.

$$\phi = \frac{\text{Energy of K-radiation emitted}}{\text{Energy of general x-radiation absorbed}}$$

The values of u have been plotted against the atomic number of the element in Fig. 3. Since the K-absorption, for any given wave-length according to the formulas given by Richtmyer[8] for absorption coefficients above and below the K-limit, is about 87 percent of the total absorption, we should expect 87 percent of the absorbed quanta to eject K-electrons and in consequence the same number of quanta of K-radiation to be re-emitted, i. e., u should by this reasoning be equal to .87. The author's results, however, are in agreement with determinations of u by Barkla[13] and by Kossel[14] from data by Sadler.[15] These have been indicated on Fig. 3 where the author's values appear as circles, Barkla's as squares and Kossel's as crosses. Moreover, as indicated near the close of the paper in the determination of the fluorescent K-radiation from the target of an x-ray tube and also of direct impact K-characteristic radiation, the use of values of ϕ based on $u = .87$ leads to an amount of fluorescent K-radiation hard to reconcile with experimental data while the use of the observed values of ϕ gives very satisfactory agreement. This points to the possibility that, at least for metals of low atomic number, only one half or less of the absorbed energy goes into photo-electric ejection of K-electrons,

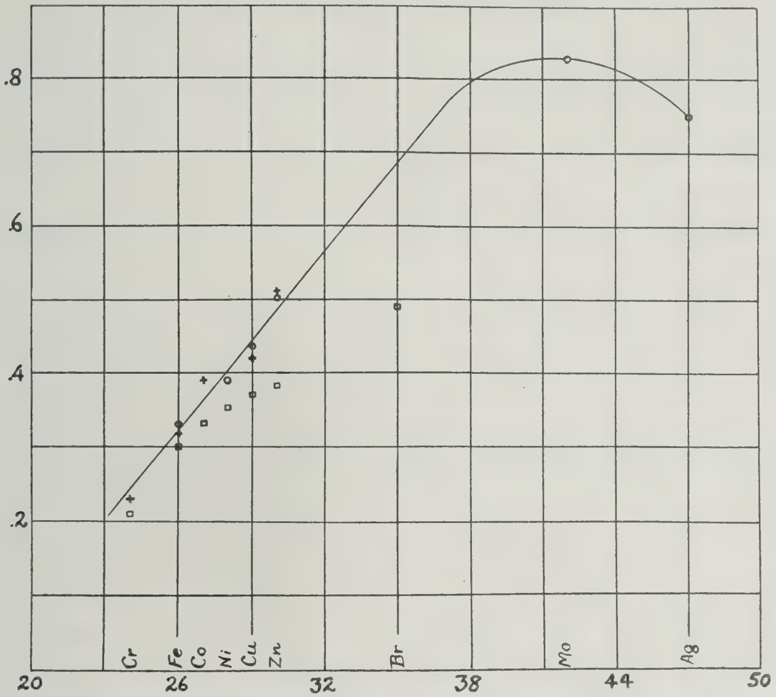

Fig. 3. Relation between ratio of quanta absorbed to quanta re-emitted and atomic number of element absorbing general x-radiation.

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[13] C. G. Barkla, Phil. Trans. **A217,** 315–360 (1918).

[14] W. Kossel, Zeits. f. Physik **19,** 333–346 (1923).

[15] C. A. Sadler, Phil. Mag. **18,** 107–132 (1909).

or else that these electrons are replaced by some process which does not involve the expected K-radiation. In this connection attention is called to the recent work of Auger[16] and of Bothe[17] indicating a "special inner absorption" of K-radiation by the parent atom, an absorption much more intense than the normal absorption by the substance, the energy leaving the atom in the form of a second ejected electron.

DETERMINATION OF INDIRECT K-CHARACTERISTIC RADIATION FROM THE TARGET

Unnewehr[18] has given some data on the ratio of the intensity of K-radiation to general radiation from the target of an x-ray tube. From a copper target at 15,400 volts the ratio between the energy of the $K\alpha$-radiation entering the ionization chamber of a simple Bragg form x-ray spectroscope and the energy of the general radiation entering simultaneously he finds to be 11.2. For a silver target at 36,400 volts he finds this ratio to be 2.7. We are now in a position to determine from fairly reliable data the ratio between the energy of indirect or fluorescent $K\alpha$-radiation entering the ionization chamber and the energy of the general radiation entering simultaneously. By comparing the two ratios we may then determine what part of the $K\alpha$-radiation measured by Unnewehr was fluorescent in origin, i. e., energy re-emitted by atoms of the target which have lost K-electrons by absorption of general x-radiation from other portions of the target. We will assume a general radiation curve I *vs* λ where, per unit volume of the target, I is the energy radiated having wave-length within a given range λ to $\lambda+\Delta\lambda$. We will further assume the mean depth of production of I to be given by the Whiddington law of electronic penetration—the depth at which the electron will have the same energy as the mean energy of the quantum of I. Since an error of 50 percent in the assumed depth of production will make a difference of only about 5 percent in the corresponding value determined for the fluorescent radiation this assumption of mean depth of production though not exact will certainly not cause a very large error in our results. The values of the penetration coefficients determined by Terrill[6] were used in the following work. It is now a simple matter to set up an expression for the energy of general radiation in a given wave-length range λ to $\lambda+\Delta\lambda$ from one elementary volume, $d\tau$, of the target which is absorbed in another element $d\tau'$. Multiplying this value by ϕ, the fluorescent energy transformation coefficient from the curve of Fig. 2 gives the resulting fluorescent K-radiation from the second element, $d\tau.'$ A portion of the resulting radiation lies within the very small solid angle $\delta'\omega$ necessary for reflection from the crystal—this quantity must then be corrected for absorption in reaching the surface of the target. A further correction factor R for absorption in air, reflection coefficient of the crystal, incomplete absorption in the ionization chamber, etc., is introduced. Its exact form is immaterial since identical corrections will apply to the general radiation entering the chamber with the K-radiation. It remains to integrate $d\tau'$ over that part of the target which contributes K-radiation to the beam reflected by the crystal and $d\tau$ over the layer of the target in which the general radiation of range λ to $\lambda+\Delta\lambda$ originates. Since the Kα-radiation is 5/6 of the total K-radiation[18] we have for the energy of fluorescent Kα-radiation

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[16] P. Auger, Comptes Rendus **180,** 65–68 (1925).

[17] Von W. Bothe, Phys. Zeits. **26,** 410–412 (1925).

[18] E. C. Unnewehr, Phys. Rev. **22,** 529–538 (1923).

$$E_{K\alpha}=\sum\frac{5}{6}\phi_n\frac{\delta'\omega}{4\pi}\,\frac{\mu_n I_n t R}{4\pi}\int_{hs} ds\int_{-\infty}^{\eta d}dx\int_0^{2\pi}d\theta\int_0^{\infty}dr\frac{re^{-\mu_n\sqrt{r^2+x^2}}}{r^2+x^2}e^{-\mu_k\epsilon(\eta d-x)} \quad (2)$$

The summation is over all wave-length ranges $\Delta\lambda$ for λ less than the wave-length of the K-absorption limit of the target. $d\tau=ds\,dx$ and $d\tau'=t\,r\,dr\,d\theta$. ηd is the depth of $d\tau$ below the surface. $\epsilon(\eta d-x)$ is the path of secondary x-rays from $d\tau'$ to the surface. s is the slit-width of the narrower slit of the collimator. h is the height of section of the focal spot of the target. By a change of variable $u=\mu\sqrt{r^2+x^2}$ this reduces to

$$E_{K\alpha}=\frac{5}{6}\,\frac{\delta'\omega}{4\pi}\,\frac{thsR}{2}\sum\phi_n\mu_n I_n\int_{-\infty}^{\eta d}-Ei(\mu x)e^{-\mu_k\epsilon(\eta d-x)}\,dx \quad (3)$$

Tables for the Ei function are given by Glaisher.[19] We wish to compare $E_{K\alpha}$ with the energy of the general radiation entering the ionization chamber at the same time. If we have so chosen $\Delta\lambda$ that it is equal to the complete range of wave-lengths entering the ionization chamber when it is set on the peak of the Kα line we may designate the value of I for this band I_G. The energy from an element $d\tau$ will then be $I_G d\tau$. The energy reaching the ionization chamber is given by

$$E_G=\int RI_G\frac{\delta'\omega}{4\pi}\,\frac{\delta\theta}{\Delta\theta}e^{-\mu'\epsilon\eta d'}d\tau \quad (4)$$

where $\delta\theta$ is the angle subtended at $d\tau$ by the slits of the collimator, $\Delta\theta$ is the maximum value of $\delta\theta$, $\epsilon\eta d'$ is the mean path of x-rays before emergence from the target, and $\delta\theta$ and $\Delta\theta$ may be expressed in terms of the dimensions of the collimator and its distance from the target. The ratio $E_{K\alpha}/E_G$ has been calculated for copper and silver from the above expressions.

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[19] J. W. L. Glaisher, Phil. Trans. **109**, 367–387 (1870).

Assuming similar ideal general radiation curves for silver at $V=36{,}400$ volts and copper at $V=15{,}400$ volts in each case with the "cut off" point as prescribed by the condition $h\nu_{max}=Ve$ and the peak at the position $\nu=\nu_{max}/1.5$ we have the following for the two ratios

$$\frac{E_{K\alpha}}{E_G}=\frac{\text{Expected indirect K-radiation}}{\text{General radiation entering ionization chamber with it}}.$$

For copper $E_{K\alpha}/E_G=5.03/.54=9.3$. Unnewehr finds this ratio 11.2 so that we have accounted for about 83 percent of the Kα-radiation. For silver $E_{K\alpha}/E_G=12.6/4.8=2.62$. Unnewehr finds this ratio to be 2.7 so that in the case of silver we have accounted by this method for 97 percent of the Kα-radiation.

The discrepancy between the results for the two metals suggests that direct impact characteristic radiation may play a more important role in the case of copper than it does in the case of silver.

ESTIMATE OF DIRECT IMPACT K-CHARACTERISTIC RADIATION FROM THE TARGET

A relative measure of the direct impact K-radiation is given by the probability that an electron of given initial velocity will approach close enough to a K-electron, before its energy has been reduced below the K-quantum, to lift it entirely out of the atom. This is the condition for direct K-characteristic radiation. To satisfy this condition the path of the electron must lie within a distance p of the K-electron where p is given by the expression[20]

$$h\nu_k=\frac{E}{1+p^2E^2/e^4} \tag{5}$$

where $h\nu_k$ is the energy necessary to lift out the K-electron, E is the energy of the impacting electron, and e is the electronic charge.

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[20] It may be shown that if a body of mass m and charge e moving with velocity v approaches another body of mass m and charge e at rest that the second body will acquire a velocity u given by

$$u=v/\sqrt{1+(p^2/e^4)(\tfrac{1}{4}m^2v^4)} \tag{6}$$

where p is the perpendicular distance from the line of flight of the first particle to the second. This is derived by the mechanics of two bodies acting by the inverse law of force. Squaring and multiplying each member by $\tfrac{1}{2}m$ and setting $\tfrac{1}{2}mv^2=E$ and letting the energy acquired by the second body be $\tfrac{1}{2}mu^2=h\nu_k$ we have Eq. (5) above. The author is indebted to Prof. Bergen Davis for Eq. (6).

For an impacting electron of a given initial energy E_0 the probability that it will lift out a K-electron is clearly the ratio of the sum of the areas of all circles of radius p about the K-electrons to the total area of the target face. The value of this ratio is

$$2\pi n\frac{e^2}{\beta}\left[\frac{2V_0-V_k}{V_k}-\log\frac{V_0^2}{V_k^2}\right] \tag{7}$$

where β is the Whiddington coefficient of penetration in the expression $V_x^2=V_0^2-\beta x$, V_0 is the energy in abvolts of the penetrating electron, V_K is the energy just sufficient to lift out a K-electron. e is the electronic charge, and n is the number of atoms per cc in the target.

Substituting appropriate values for the two cases investigated above, silver at $V_0=36{,}400$ volts gives .00028 and copper at $V_0=15{,}400$ volts gives .00108. We should expect then about four times as many quanta of direct K-radiation from copper at 15,400 volts as from silver at 36,400 volts. In terms of energy we should expect 1.4 times as much energy from the copper as from the silver. In view of this it seems obvious that the greater part of the K-radiation is not direct impact radiation as Beatty claims for how then explain that the observed ratio of Kα-radiation of copper and silver for the above voltages is 6 to 13 when from the calculation above it should be 1.4 to 1? On the other hand we now can explain the fact that our calculated value for the Kα-line of copper was too low if for metals of low atomic number the direct K-radiation forms a considerable part of the total K-radiation but for metals of high atomic number the direct radiation becomes relatively of much less importance. This may be the explanation for the failure of molybdenum and silver to show increase in radiating efficiency in the curves for total energy as found by Brainin.

Returning to Unnewehr's data and our calculated values of Kα-radiation we have the following:

TABLE III

Target	Cu	Ag
Tube voltage	15,400	36,400
Total Kα-radiation (Unnewehr)	6.0	13.0
Indirect (fluorescent) Kα-radiation	5.03	12.6
Difference = direct impact Kα-radiation	1.0	.4

The ratio 1.0/0.4 = 2.5 is in good agreement with the expected value 1.4.

As suggested above we may now make use of these results to check the validity of our determination of ϕ, the fluorescent energy transformation coefficient. If we use in place of ϕ in the calculation of indirect K-radiation from the target a value of the transformation coefficient derived from the assumption that $u=.87$ we shall have to substitute in Table III above 10.1 and 14.6 for the energy of the fluorescent Kα-radiation of copper and silver respectively. These values are actually larger than the total Kα-radiation observed by Unnewehr and copper now shows relatively more indirect radiation than silver. This leaves no room for any appreciable amount of the direct impact radiation which seems necessary to explain Brainin's results referred to in the preceding paragraph. These facts then seem to point to the reliability of the observed values of u as given in Table II.

CONCLUSIONS

It seems established that for any given element the ratio between the number of quanta of x-rays of any wave-length absorbed to the number of quanta of secondary K-characteristic x-rays emitted is a constant. Experimental values indicate that this quantum transformation coefficient is much less than unity and increases markedly with atomic number. This increase is further indicated by the comparison of calculated with observed values of K-radiation from the target of an x-ray tube. For copper and probably other elements of low atomic number a considerable part, but probably much less than fifty percent, of the K-radiation originates from direct impact of the cathode electrons. For silver on the other hand, and probably other elements of high atomic number, a very small part of the total K-radiation has such an origin.

I wish to express my appreciation for the interest and help of Professor Bergen Davis who suggested this research and under whose direction it was performed. Grateful acknowledgement should also be made to the Westinghouse Laboratories at Bloomfield, N. J. for the water-cooled tungsten tube used in the research.

PHOENIX PHYSICAL LABORATORIES,
COLUMBIA UNIVERSITY,
February 1, 1926.

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A SPECTROGRAPHIC EXAMINATION OF THE STRIATED DISCHARGE IN MIXED GASES*

By David A. Keys and M. S. Home

Abstract

The present paper contains the results of a spectroscopic examination of the striated discharge in (1) a mixture of nitrogen and hydrogen, (2) a mixture of helium and hydrogen. Spectrograms were taken of the light emitted by the negative glow and by the striations respectively. The electronic energies in the different regions of the discharge are interpreted from these spectra in much the same manner as that first suggested by Seeliger and now used by astrophysicists to determine the extent of ionization in different stars and in various levels of the sun's atmosphere from the spectra of their regions. In the nitrogen mixture the Balmer lines and the nitrogen bands 4708, 4278 and 4236 were found to appear in the negative glow but to be absent from the striations. Interpreting this result in terms of electronic energies (or equivalent quanta, if radiation) there are relatively few electrons possessing energy equivalent to 15.5 volts in the striations though the potential applied to the discharge tube was about 1100 volts. In the mixture of helium and hydrogen, the Balmer lines are strong in the striations but relatively weak in the negative glow. The line spectrum of helium was strong in the negative glow but weak or absent in the striations. The mercury arc lines were equally strong in both parts of the discharge. In terms of electronic energies, these results mean that there are relatively few electrons possessing energy equivalent to 25.3 volts in a striation but plenty possessing energies of 10.4 and 15.5 volts. An explanation is suggested of the change in intensity of certain lines in mixtures of different gases.

THE following experiments are a continuation of a former paper,[1] in which the spectra from the different regions of a striated discharge are examined with a view to determining (I) the relative concentration of the different atoms and molecules in the various excited states and (II) the distribution of potentials or electronic energy in the same regions. The distribution of potential and the electric field in different parts of a striated discharge have been measured by many investigators. The various methods which have been used may be classified under the following four groups: (A) the exploring electrode,[2] (B) the cathode ray beam,[3] (C) the Stark effect,[4] (D) the hot and cold sounding probe method due to Langmuir.[5] The unreliability of A and the limitations of B and C are quite evident. The presence of the probe in those experiments in which the Langmuir method has been used, has been found not to distort the field appreciably. In these cases the current density has been comparatively large. But in discharges of small current densities such as are used in the present paper any obstruction in the path of the discharge is more liable to alter conditions. Moreover, under the conditions of the experiments to be described, the discontinuities in the current potential curves obtained by the Langmuir method would be very difficult to designate with accuracy. The method adopted in this paper was therefore similar to that used by Seeliger,[6] who observed the variation in intensity of certain spectral lines in different regions of a glow discharge. The light emitted by different regions of the discharge was photographed with a spectrograph and from the nature of the spectra the potentials or electronic energy necessary to produce the lines determined.* The gas is thus made to reveal its own condition and the potentials are determined in much the same manner as that used by astrophysicists[7] to determine the extent of ionization among the different atoms in the various stars and in the different depths of the stellar atmosphere of the same star, by examining the light which they emit or absorb. The method is limited by our knowledge of excitation and ionization potentials but some information may be obtained when these potentials are known. One of us has already pointed out some differences in the spectra from different parts of a single striation and the negative glow in the case of hydrogen.[1] The present paper contains the result obtained from the examination of (i) a mixture of nitrogen and hydrogen and (ii) a mixture of helium and hydrogen.

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* Read in abstract, Kansas City Meeting of the American Physical Society, December, 1925.

[1] D. A. Keys, Trans. Roy. Soc. Canada **19,** 143 (1925).

[2] J. J. Thomson, "Conduction of Electricity through Gases." 2nd Edition p. 528.

[3] J. J. Thomson, Phil. Mag. **18,** 441 (1909); F. W. Aston, Proc. Roy. Soc. A.

[4] E. Brose, Ann. d. Physik **58,** 731 (1919).

APPARATUS

The apparatus used was similar to that described in an earlier paper,[1] consisting of a glass tube about 95 cm long and 5.5 cm in diameter, fitted with parallel plane aluminium electrodes. The potential difference between the electrodes was about 1100 volts and the current about 10 milli-amps. supplied by an Evershed and Vignolles direct current generator. The spectrograms were taken with a Hilger constant deviation glass spectrograph. The tube was exhausted by a Hyvac oil pump and a charcoal tube cooled with liquid air. The gases were dried with phosphorus pentoxide and the discharge tube was washed out thoroughly several times with the gases before a photograph was taken, the discharge passing through each rinsing in order to remove as much as possible of the "residual" gases from the electrodes. No attempt was made to bake the tube or the electrodes.

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[5] I. Langmuir, J. Frankl. Inst. **196,** 751 (1923).

[6] R. Seeliger, Ann. d. Physik **67,** 352 (1922).

* It has been suggested to the authors that the Langmuir probe method might have been used to measure the velocity distribution and thus directly test the relation suggested. We hope to try this later.

[7] Saha, Proc. Roy. Soc. **A99,** 136 (1924).

OBSERVATIONS

Nitrogen and hydrogen. The nitrogen was prepared by heating a solution of potassium nitrite and ammonium chloride, the gas being purified by passing it over heated copper turnings to remove any trace of oxygen present and over phosphorus pentoxide to remove the water vapor. Some observations were first made on the relation between the current and the applied potential. It was found that at a certain potential the current rose rapidly without any change in potential, the pressure of the gas being about 0.01 cm of mercury. On reducing the potential the current did not fall to its former value, confirming Olsen and Young's observation,[8] who attribute this fact to the charging up of the walls of the tube. The potential was then kept constant at about 1100 volts and spectrograms were taken of the light emitted by the negative glow and by a striation. The results are shown in Fig. 1. It will be seen that the lines Hα and Hβ come out strongly in the negative glow but are absent in the striation. To produce the Balmer lines from molecular hydrogen requires 15.5 volts and to produce the negative bands in nitrogen requires 17.75 volts.[9] *It therefore appears that there are no electrons present in the striation possessing energy equal to 15.5 volts, though the potential between the ends of the tube is 1100 volts.* If we assume a Maxwellian distribution for the energy of electrons, the results show that the center of this

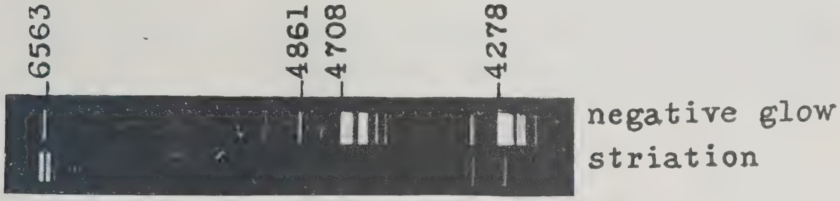

Fig. 1. Spectrogram of the striated discharge in a mixture of nitrogen and hydrogen.

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[8] A. R. Olsen and T. F. Young, Phys. Rev. **25,** 58 (1925).

[9] E. E. Witmer, Phys. Rev. **26,** 780 (1925).

distribution corresponds to an energy less than 15.5 volts in the striation.

Helium and hydrogen. Helium with a small trace of hydrogen was now used in the tube. Some interesting changes in the nature of the discharge were noticed during this washing. When the striations were first formed they were not equally spaced, the distance between the striae near the anode being only about one-half that between those near the cathode. A stria would appear to vanish in the middle of the positive column without any visible effect on its neighbors. The phenomenon lasted about a minute and was not observed in any subsequent work. This effect is attributed to nitrogen liberated by the electrodes. On commencing the discharge the striae were formed at once but were not clearly defined. After about ten minutes they became quite sharp but in an hour they commenced to degenerate into the continuous positive column and after two hours the column was continuous except for two striations near the cathode end. The current was then raised from 10 to 12 milli-amps. and in a few minutes the striae returned to their former sharpness. This was repeated several times during each washing. No visible change in pressure could be detected with the McLeod gauge during this degenerating process. All traces of nitrogen were finally removed and after leaving the tube connected for three hours with the charcoal tube cooled with liquid air, the discharge settled down to a steady state, a trace of mercury vapor and hydrogen being the only impurities present. A typical spectrum of the negative glow and of a striation is shown in Fig. 2. Table I gives some of the principal lines and their relative intensities measured in these photographs. The notation is that used by Fowler.[10]

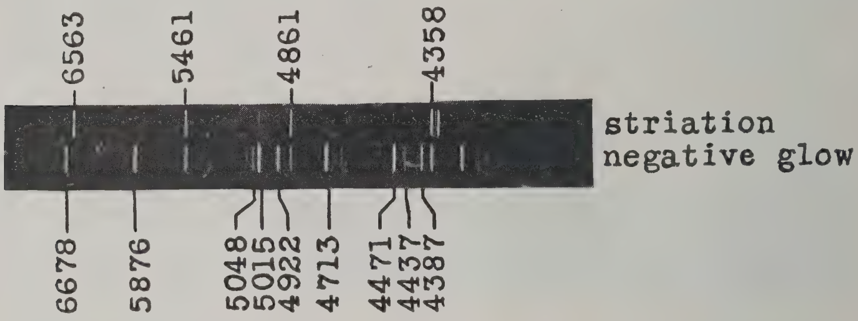

Fig. 2. Spectrogram of the striated discharge in a mixture of helium and hydrogen.

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[10] A. Fowler, "Report on Series in Line Spectra."

The table shows that the line spectrum of helium is strong in the negative glow but it is practically absent in the striation, the only series which show any tendency to persist being the $1S-mP$ and $1\pi-m\delta$.

From these sepectrograms we see that the helium lines are strong in the negative glow and very weak or absent in the striation. The hydrogen Balmer lines however are strong in the striation and weaker in the negative glow. This is just the reverse of what is the case when hydrogen alone is used.[1] The mercury lines 5461, 4358 and 4047 are equally strong in both parts of the discharge. Interpreting these results in terms of electronic energies, *we see that relatively few electrons have energy equivalent to 25.3 volts in the striation but that a large number have energy equivalent to 10.4 volts* (*to produce the mercury lines*) *and 15.5 volts to produce the Balmer lines.*

TABLE I

Lines in the spectra of the negative glow and of the striations. Helium and hydrogen mixture.

Series type	Wave-length	Negative glow	Striation
$1S-2P$	5015	Strong	Fairly strong
$1S-3P$	3965	Weak	Absent
$1P-2D$	6678	Strong	Very weak
$1P-3D$	4922	Strong	Very weak
$1P-4D$	4387	Strong	Very weak
$1P-5D$	4144	Weak	Very weak
$1P-3S$	5048	Strong	Absent
$1P-4S$	4437	Strong	Absent
$1\pi-2\delta$	5876	Strong	Weak
$1\pi-3\delta$	4471	Strong	Weak
$1\pi-4\delta$	4026	Strong	Absent
$1\pi-3\sigma$	4713	Strong	Very weak
$1\pi-4\sigma$	4120	Weak	Absent
Hα	6563	Very weak	Strong
Hβ	4861	Fairly strong	Strong
Hg	5461	Strong	Strong
	4358	Strong	Strong
	4047	Strong	Strong

In contrast to the behavior of hydrogen in nitrogen, the Balmer lines Hα and Hβ in the mixture of hydrogen and helium are much fainter in the negative glow than in the striation. Furthermore, the two lines in the latter case show a curious reversal of intensity in the negative glow. Hα is very faint while Hβ is much stronger though the normal intensity of Hα is greater than that of Hβ. It appears that the presence of helium in some way prevents the excitation of these two Balmer lines in the negative glow and enhances them in the striations. Merton and Pilley[11] have shown that the presence of helium at high pressures increased the intensity of the N^+ lines in the positive column and McLennan and Shrum[12] found that the presence of helium or neon brought out the famous green line 5577 in oxygen. Now we have shown that the Balmer lines are affected in the same manner, and the same explanation may be applied to their experiments as to ours, namely that the inert gases cause a redistribution of the electronic energy so that the maximum energy occurs in a region which will excite these lines in all three cases just cited. Compton[13] has given an explanation of Merton and Pilley's results as being due to optical excitation by collisions of the second kind. According to the theory of Klein and Rosseland, the probability of such excitation taking place decreases as the difference between the energy of the excited atom and that required to excite the second atom increases. The difference between the excitation potential of $H\alpha$ and $H\beta$ is very small, and, though the probability of $H\beta$ being optically excited by the excited or ionized helium in the negative glow is greater than that of $H\alpha$, the difference in this probability seems hardly sufficient to account for the result that $H\beta$ is so much stronger than $H\alpha$. Hughes and Klein[14] have shown that the fraction of the collisions of electrons with atoms and molecules which result in *ionization* increases to a maximum and then decreases as the energy of the electrons increases. On the supposition that the $H\alpha$ and $H\beta$ lines are excited directly for the most part by electrons, this reversal of intensity of $H\alpha$ and $H\beta$ in the negative glow would mean that the Maxwellian distribution of energy among the electrons in the negative glow has a maximum which has a higher energy value that that required to excite the $H\alpha$ line. In a discharge tube using a hot cathode and a mixture of mercury vapor and hydrogen, Turner and Compton[15] have shown that the arc spectrum of mercury is emitted both from the negative glow and from a striation, and Compton, Turner and McCurdy[16] found no trace of the hydrogen lines in the striations in a similar experiment, while the Hg bands were found in the striations. This is a result similar to the behavior of hydrogen as found in our experiments. Work is being continued using still larger discharge tubes and different gasseous mixtures to see how the distribution is affected by the diameter of the tube, the different gases present and their relative concentrations.

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[11] T. R. Merton and J. C. Pilley, Proc. Roy. Soc. **A107,** 411 (1925).

[12] J. C. McLennan and J. M. Shrum, Proc. Roy. Soc. **A 108,** 501 (1925).

[13] K. T. Compton, Phil. Mag. **50,** 512 (1925).

[14] A. L. Hughes and E. Klein, Phys. Rev. **23,** 450 (1925).

[15] L. A. Turner and K. T. Compton, Phys. Rev. **25,** 606 (1925).

[16] K. T. Compton, L. A. Turner and W. H. McCurdy, Phys. Rev. **24,** 597 (1924).

CONCLUSION

1. Spectrograms have been taken of the negative glow and of a striation in mixtures of (i) nitrogen and hydrogen (ii) helium and hydrogen.

2. In the case of the nitrogen mixture, the Balmer lines Hα and Hβ and the nitrogen bands 4708 and 4278 appear in the negative glow, but are absent from the striation.

3. In a mixture of helium and a trace of hydrogen the helium line spectrum is strong in the negative glow but weak or absent in the striations. The hydrogen lines are strong in the striations but relatively weak in the negative glow. The mercury lines are strong in both parts of the discharge. Hα is much weaker than Hβ in the negative glow.

4. A method of interpreting the electronic energies in different parts of the discharge from the spectra emitted has been followed. On this hypothesis there are relatively few electrons possessing energy equivalent to 15.5 volts in the striations in the nitrogen mixture. Also in the case of the helium mixture, a relatively small number of electrons have energy equivalent to 25.3 volts, but there are plenty with energies equivalent to 10.4 and 15.5 volts in a striation.

5. An explanation of this change in the distribution of the intensity of certain lines in mixtures of gases is suggested on the supposition of a change in the position of the peak of the Maxwellian distribution of energy among the electrons.

THE MACDONALD PHYSICS BUILDING,
MCGILL UNIVERSITY,
February 15, 1926.

THE FORMATION OF NEGATIVE IONS IN MERCURY VAPOR

By Walter M. Nielsen

Abstract

The method used is similar to that of Mohler. Electrons, projected along the axis of a tube between two plates were prevented from scattering by a magnetic field of 350 gauss parallel to the axis of the tube. Negative ions formed by the attachment of an electron to an atom or to a molecule were removed by suitable potentials applied to the side plates. The remainder of the current reached a circular plate at the end of the tube. With a small field between the side plates, the negative ion current was just barely observeable (1×10^{-10} amperes). With higher fields the ion current increased enormously, approaching saturation when the potential difference between the side plates was increased to between 3 and 4 volts. In this report the ion currents were of the order of 9×10^{-9} amperes. The total current was of the order of 1×10^{-7} amperes.

The ratio between the negative ion and total current decreases with increase in the driving potential for low voltages, but increases at 2.7, 4.7, 5.5, and 8.8 volts. The decrease at low potentials is similar to the results of Mohler in other gases and vapors. The cause of the break at 2.7 volts is not known. The breaks at 4.7, 5.5, and 8.8 volts are believed to be associated with the electronegative properties of the mercury atom having an electron in a metastable orbit. The total current rises rapidly with increase in the driving potential and decreases at 4.9 and 6.7 volts.

Introduction

F. L. MOHLER[1] has recently published a report on the production of negative and positive ions in a number of vapors and gases including mercury vapor. He projected a beam of electrons along the axis of a cylinder in an approximately equipotential region with a magnetic field of 100 gauss parallel to it. He then applied a positive or negative potential of one volt to the cylinder, measuring in each case the negative or positive current to it. He concluded that under the conditions of his experiment, the number of negative ions formed at low pressure was small compared to the number of positive ions formed above the ionization potential. No negative ions were observed in mercury vapor for impinging electrons having speeds less than 10.4 volts.

The present investigation is concerned with a somewhat similar attempt to study the formation of negative ions in mercury vapor. Under conditions which are believed to approximate those in the above work, similar results were obtained, but under different conditions, results were obtained which are regarded as evidence for the existence of negative ions of mercury vapor.

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[1] F. L. Mohler, Phys. Rev. **26**, 614–624 (1925).

EXPERIMENTAL APPARATUS

The apparatus and electrical circuit are shown in Fig. 1. Electrons from a filament F were projected along the axis of a Pyrex tube by means of a potential V_F between the filament and a diaphram C. Two plates, P_1 and P_2, were placed in a skew position as shown. Electrons were prevented from reaching them by placing the tube in the core of a solenoid so that the lines of force in the region between C and a circular plate P_3 were parallel to the axis of the tube. The intensity of the field was about 350 gauss. Outside the plates P_1 and P_2 and next the glass wall was a grounded gauze to eliminate extraneous surface potentials. All metal parts with the exception of the tungsten filament were of copper. The filament assembly was provided with a ground glass joint and mercury seal to facilitate replacement. The source of electrons was a tungsten spiral of one loop placed so that its elements were perpendicular to the axis of the tube.

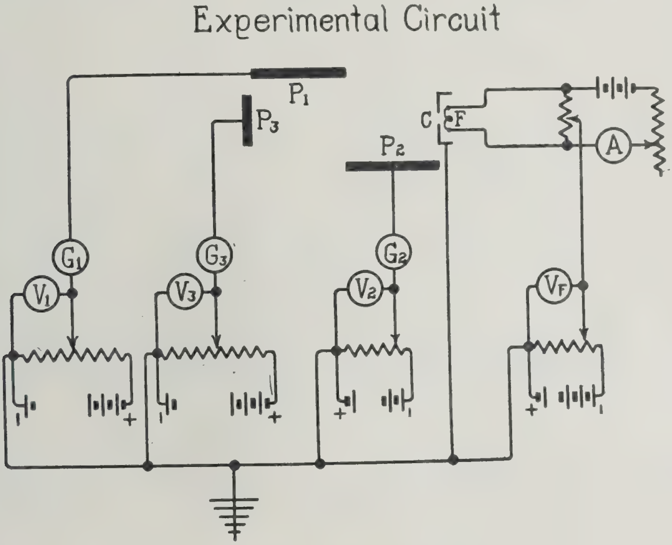

Fig. 1. Apparatus and electrical circuit.

Galvanometers and suitable sources of potential were connected to the plates P_1, P_2, and P_3. V_3 was generally a fraction of a volt higher than V_1, both being positive with respect to C. Under such conditions, electrons brought to rest as the result of inelastic collision would be attracted downward and would not therefore have a tendency to diffuse from the center of the tube as apparently occurred in the experiments of Richardson and Chaudhuri.[2] The galvanometer G_1 measured the current i_1 due to the negative charges which were able to drift to P_1 in spite of the magnetic field. This current increased rapidly with increase in the electric field between the side plates so that it was necessary to apply to them a potential difference of between 3 and 4 volts to attain saturation. The galvanometer G_2 was intended to measure the positive ion current i_2. The galvanometer G_3 measured the negative current i_3.

The vapor pressure in the tube was about .003 mm of mercury, a pressure corresponding to the temperature of the mercury seal during the observations.

Results and Discussion

With a low filament temperature, readings were taken simultaneously of i_1, i_2, and i_3, for different values of the driving potential. In most of the present work G_2 was used to indicate the ionization potential only. Dividing the current to P_1 by that reaching P_1 and P_3, a fraction R is obtained which gives the ratio between the negative ion and total current. If, as in this report, the negative ion currents are saturation currents, this number is proportional to the number of negative ions formed per unit electron current. The results are shown by the curve of Fig. 2. In this case, V_1 was 3 volts, V_3 was 3.2 volts and V_2 was zero. The potentials are corrected for initial velocity, etc., assuming the ionization potential of mercury to be 10.4 volts. The ion current was of the order of 9×10^{-9} amperes and the total current was of the order of 1×10^{-7} amperes.

The curves shown in Fig. 2, as well as those in Fig. 3 and Fig. 4 to follow, are representative of several taken over the same range under approximately the same conditions. While the currents vary somewhat because of differences in the intensity of the magnetic field, the critical points are all reproducible with the exception of a kink on the ratio curve at 7.7 volts, which did not appear on some of the curves. It did not appear on the curve of Fig. 2. It is quite astonishing that the breaks are so definite in view of the relatively large potentials on P_1 and P_3 which would be expected to blur out the effects. The fact that changes in these potentials did not produce marked changes in the critical points was proved experimentally. A change in the potential difference between P_1 and P_2 of 1 volt, lowered the value of V_F necessary to produce ionization by .1 volt.

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[2] Richardson and Chaudhuri, Phil. Mag. **45**, 337–52 (1923).

That the currents observed above are in some way due to the presence of the mercury vapor was proved by removing the vapor. Carbon dioxide snow was applied to the mercury trap while the tube and connecting glassware were heated. After a few hours it was found that the negative ion current had been reduced to such an extent as not to be detectable with the galvanometer used. That such observed currents are due to electrons which have collided a number of times is quite improbable because of the low vapor pressure and because the experimental conditions, to some extent, prevented electron diffusion. One would expect that some of the electrons deflected in such a manner would have energy corresponding to V_F. To test this point, with V_1 and V_2 equal to zero, and with V_3 equal to 1.1 volts, it was found that the current to P_1 was not detectable for all values of V_F below the ionization potential. Indeed, it must be emphasized that it was necessary that V_1 be of the order of 2 or 3 volts positive in order to attract

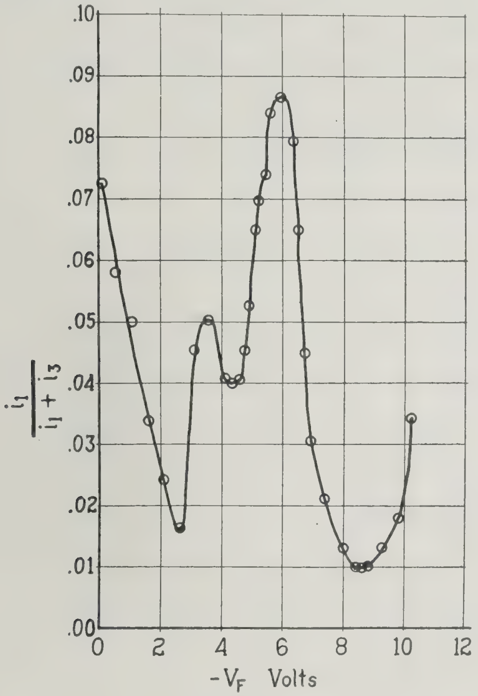

Fig. 2. Variation of the ratio of negative to total current with accelerating potential. $V_1=3.0$ volts, $V_2=0.0$ volts, and $V_3=3.2$ volts.

the negative charges to P_1 and cause currents of the order of 9×10^{-9} amperes as observed above. Whether or not Mohler's failure to observe these negative charges is due to this fact, is not known. In neither case do the electric fields lend themselves to computation. With a potential of 1 volt positive on P_1, the negative ion current was barely observable, being about 1×10^{-10} amperes. The radius of curvature of a 10 volt electron traveling initially at right angles to the axis of the tube in a magnetic field of the order used is about .6 mm. It seems unlikely, therefore, that the increased potential of P_1 would increase electron scattering to the walls. Because of the above facts, it seems necessary to believe that it is possible under certain circumstances for an electron to attach itself to a mercury atom or molecule.

The decrease in the ratio curve of Fig. 2 is similar to the effect observed by Mohler[1] in other gases and vapors. To explain this, he assumed that only slowly moving electrons attach themselves to molecules to form negative ions. At potentials equal to potentials of inelastic collision he observes an increase in the negative ion current in agreement with his theory. Accepting this view, one would expect an increase in the ratio curve at 4.9 volts in mercury vapor. That no kink was observed, may be due to the fact that the resolving power of the apparatus was not sufficient to distinguish it from an effect setting in at about 4.7 volts. The increase at 2.7 volts cannot be correlated with the critical potentials of the mercury atom. Possibly it is of molecular structure, although mercury vapor is generally regarded as monatomic. The mercury atom is known to have two metastable orbits corresponding to about 4.7 and 5.5 volts. The $2p_3$ orbit has a computed energy of 4.66 volts and the $2p_1$ orbit has a computed energy of 5.43 volts. Critical potentials at 4.68 and 5.47 volts have been observed by Franck and Einsporn.[3] There is evidence that an excited atom possesses an electron affinity and hence tends to form negative ions.[4] Because of these facts, the breaks in the ratio curve at 4.7 and 5.5 volts have been interpreted as being critical potentials for the formation of negative ions of mercury vapor. The rise in the curve at 8.8 volts may be interpreted to support that view. Franck and Einsporn[3] list a number of levels which they associate with an observed critical potential of 8.8 volts. The levels $3p_1$, $3d_1$, $3d_2$, $3d_3$, and $3P$ have computed potentials ranging from 8.79 to 8.82 volts. While some of these levels are metastable, those which are not, revert to levels of lower energy by the emission of mono-chromatic radiation. In particular, some of them will return to the $2p_1$ and $2p_3$ orbits, making the atom susceptible to the formation of a negative ion. An increase in the ratio of negative ion to total current would therefore be expected from this view-point when the impinging electron is able at collision to remove the valence electron to the $3p_1$, $3d_1$, $3d_2$, $3d_3$, and $3P$ levels. Since an additional electron is necessary for the formation of a negative ion, it seems quite possible that the impinging electron having lost all of its energy, would remain attached to the atom or molecule with which it collided.

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[3] Franck and Einsporn, Zeits. f. Physik **2,** 18–29 (1920).

[4] See for example Franck and Grotian, Zeits. f. Physik **4,** 89–90 (1921); Compton, K. T., Lilly, E. G., and Olmstead, Phys. Rev. **16,** 282–289 (1920); Davis, A. C., Proc. Roy. Soc. **100A,** 599–620 (1922).

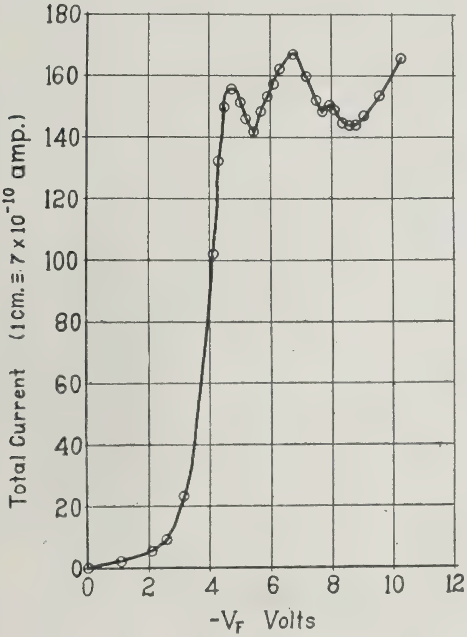

Fig. 3. Variation of total current with accelerating potential. V_1, V_2, and V_3, same as in Fig. 2.

Fig. 3 gives the variation of the total current with the driving potential. The two breaks in the curve at 4.9 and 6.7 volts correspond to the two prominent resonance potentials of the mercury atom. That the negative ions were instrumental in decreasing the total current is shown by the curves of Fig. 4, which show the variation in the total current for different positive potentials on P_3. In A, V_3 was 0 volts, in B, V_3 was 1.1 volts, and in C, V_3 was 3.2 volts. The fact that curve A shows no breaks may be attributed to the fact that possibly under such conditions very few of the electrons have energies corresponding to V_F because of space charge. With higher values of V_3, such as with B and C, the total current rises more rapidly but then seems to drop off in the region in which large numbers of slowly moving ions are formed. If now a potential is applied to P_1, such as in curve D of Fig. 4 and in the curve of Fig. 3, the total current is enormously increased, particularly in the region of 5 and 6 volts. In the case of curve D, Fig. 4, practically none of the negative ions reached P_1, although apparently some of them have been removed to a more ineffective part of the tube.

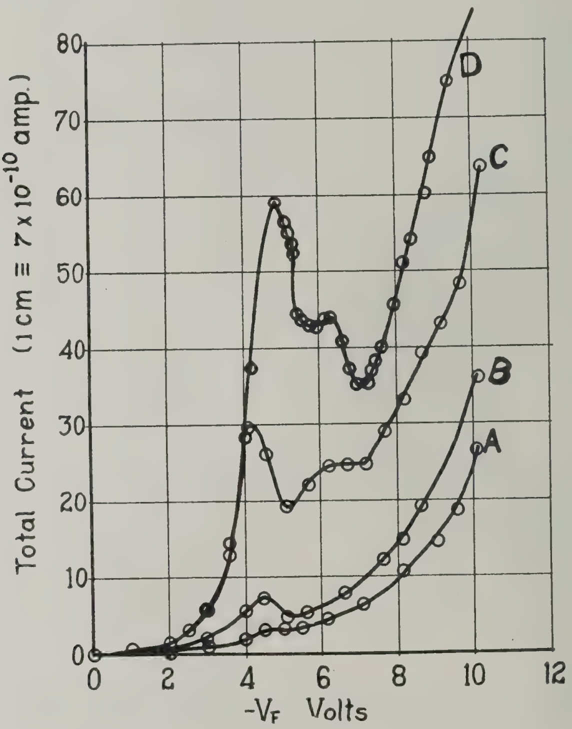

Fig. 4. Variation of total current with accelerating potential. $V_1=0.0$ volts, $V_2=0.0$ volts, in A, B, and C. In A, $V_3=0.0$ volts, in B, $V_3=1.1$ volts, and in C, $V_3=3.2$ volts. In D, $V_1=1.1$ volts, $V_2=0.0$ volts, and $V_3=3.2$ volts.

The drop in the curve at 5.5 volts may be associated with the increase in the ratio curve of Fig. 2 at about this potential. In the case of Fig. 3, however, the abrupt increase in the total current at this potential as well as at 8.8 volts are difficult to reconcile with the present interpretation of the data.

It is hoped that work now in progress with a tube of greater resolving power will furnish additional information on the current voltage characteristics of the electron beam and on the nature of the break at 2.7 volts.

The writer acknowledges with pleasure the encouragement and advice of Professor John T. Tate.

Physical Laboratory,
University of Minnesota,
February 9, 1926.

PROBABILITY OF IONIZATION OF GAS MOLECULES BY ELECTRON IMPACTS. II CRITIQUE

By K. T. Compton and C. C. Van Voorhis

Abstract

Corrections to results of Hughes and Klein. Three sources of error are found and approximate corrections for them determined. They are (1) an effect of the electric field on the effective area of holes in the grid through which the primary electrons pass, which introduces corrections varying from −18 percent at the lowest voltages to +14 percent at 300 volts; (2)presence of slow secondary electrons and lack of uniform velocity of electrons in the primary electron stream, which necessitate additive corrections ranging from 30 to 50 percent; (3) warming of the gas by the filament, necessitating an additive correction of 12 percent. *Correction to our previous results.* Owing to lack of uniformity of velocities of electrons in the primary electron stream, we must add corrections of 24 percent at 45 volts, 11 percent at 100 volts and 9 percent beyond 125 volts. With these corrections the results from these two sets of experiments are in fair agreement. Curves show the final values for the probability that an ionizing collision will be made in a cm path in the gas at 0.01 mm pressure and 25°C by an electron of any speed up to 400 volts in He, Ne, A, H_2, N_2, Hg, HCl, and also for the probabilities of ionization at an impact in these gases.

SEVERAL attempts have been made to measure directly the average ionization per centimeter path by an electron moving with known speed through a gas at definite pressure, leading to calculations of the probability of ionization at a collision as a function of the speed of the electron and the nature of the gas. Of the three recent investigations of this subject, two[1] are in qualitative agreement with each other and with earlier work,[2] while the third[3] presents unique results. The present paper is devoted to an investigation of sources of error inherent in the methods which have been used and to the correction of previous results.

In our earlier paper we pointed out that our values for probability of ionization could hardly be too large, owing to the rather direct method of making the measurements. Since the values reported by Hughes and Klein were much smaller than ours (25 to 40 percent), we constructed and tested an apparatus built to duplicate as nearly as possible the essential features of their apparatus and found inherent in their method two considerable sources of error which, together with a third error mentioned in our preceding paper, explain the low values obtained by them. The filament F, grid G and plate P were similar to the electrodes used by Hughes and Klein, but the collector C was added for reasons which will be apparent. In particular the holes in the grid were made of the same size as those in Hughes and Klein's apparatus.

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[1] Hughes and Klein, Phys. Rev. **23,** 450 (1924); Compton and Van Voorhis, Phys. Rev. **26,** 436 (1925).

[2] Lenard, Ann. der Physik. **12,** 474 (1903); **15,** 484 (1904); Kossel, Ann. der Physik **37,** 393 (1912); Mayer, Ann. der Physik **45,** 1 (1914).

[3] Jesse, Phys. Rev. **26,** 208 (1925).

Hughes and Klein measured the ionization by the positive ion current to P when a field V_1 greater than the accelerating field V_a was applied to prevent the primary electrons from the filament from reaching it. In order to measure the primary current through the grid, they reversed the field V_1 into the direction V_2 and measured the electron current to P. This current increased slowly linearly with V_2 for values of V_2 greater than V_a, and they assumed that by extrapolating this back to the field V_1 they would find the primary current through the grid for the field V_1.

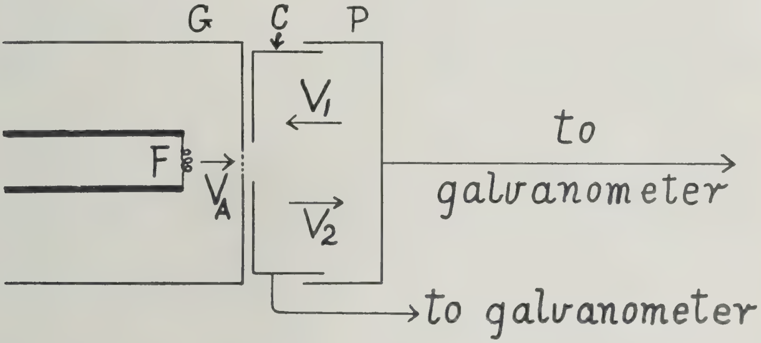

Fig. 1. Apparatus for measuring probability of ionization by the method of Hughes and Klein. The collector C was added to permit measurement of primary electron current.

Now this variation of electron current to P with V_2 is due in part to the action of the field on the *effective open area of the holes in the grid.* In other words, a large field V_2 will pull through the holes some electrons which, with smaller fields, would have struck the grid near these holes. A consideration of the geometry of the electric field near such holes suggested that the relation between current and field V_2 should be nearly linear *only for large values of* V_2 and that linear extrapolation through $V_2=0$ to the oppositely directed V_1 is unjustifiable.

To measure the error introduced by Hughes and Klein's extrapolation method, we measured directly the primary current through the grid, with the field V_1 just so large that no electrons reached P, by measuring the current to C which was kept at the same potential as the grid G. Then with the same fixed value of accelerating field V_a, the current to P was measured for various values of field V_2, as was done by Hughes and Klein. The results are shown in Fig. 2 in which A is the direct measurement whereas B is the value which would have been taken by the extrapolation method of Hughes and Klein. It should be noted that the direct measurement is too small, because some of the primary electrons return again through the hole in C and are not detected. The hole in C had an area of about 10 percent of the whole area of C and we think that 15 percent is probably an upper limit to the fraction of the primary electrons which thus escape. Thus the true primary current effective in the ionization experiments should be about that indicated by P instead of B. Similar tests were made at various accelerating fields V_a. The curve I of Fig. 3 indicates the approximate corrections which should be made to Hughes and Klein's results at various voltages to take account of this source of error.

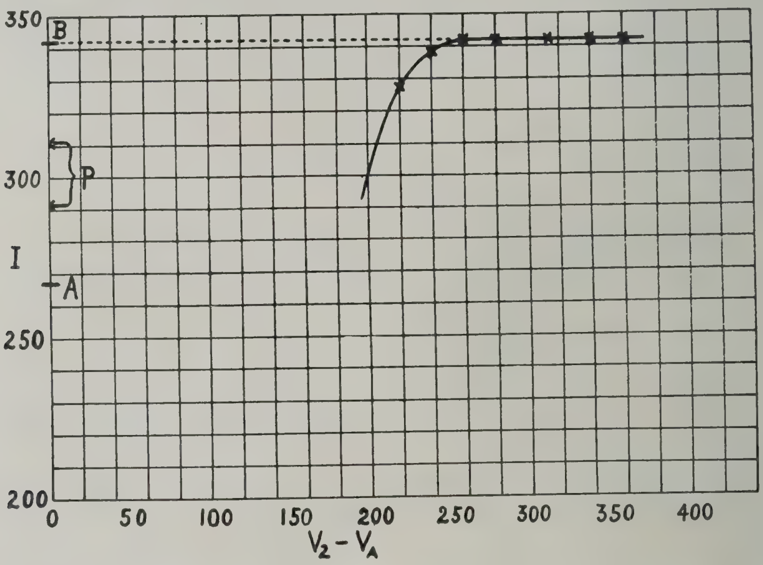

Fig. 2. Effect of retarding or accelerating field on the number of electrons passing through the holes in G. A is the actual primary electron current with sufficient retarding field to prevent electrons from reaching plate. P is this current corrected for loss through the hole in C. B is the current as estimated by Hughes and Klein.

Considerably more serious is an error due to the fact that the primary electron stream, thus measured, contains a large proportion of slow secondary electrons from the grid, which contribute little or nothing to the ionization. The existence of large numbers of slow secondaries in this type of apparatus was demonstrated recently by Lehman and Osgood.[4] We made tests of the distribution of velocities of the electrons passing through the grid, by measuring the current to P for various retarding fields V_1 between 0 and V_a, and repeated this at various values of the accelerating field V_a. Without showing these curves, the following results may be stated as clearly indicated: (1) There is an ineffective group of secondaries amounting to about 15 percent at 50 volts, 22 percent at 98.5 volts, 33 percent at 151 volts, 40 percent at 202 volts and 42 percent at 290 volts. (2) The remaining effective group of electrons at each accelerating voltage is fairly homogeneous,

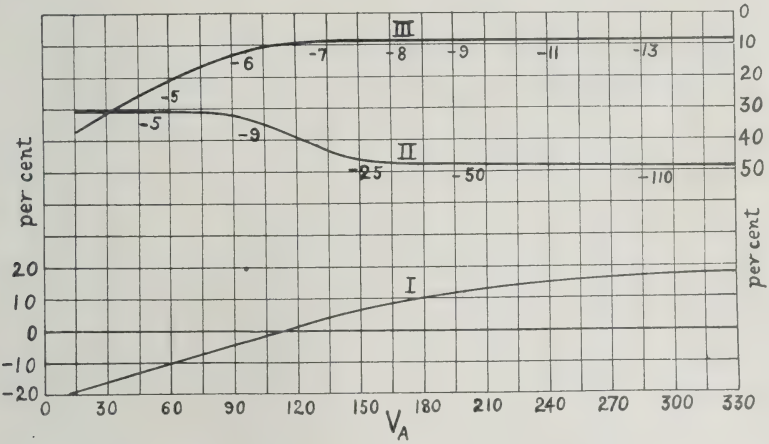

Fig. 3. Curve I gives corerctions to be applied to results of Hughes and Klein on account of the effect of the field on the number of electrons passing through the grid. Curve II gives the corrections to results of Hughes and Klein due to inhomogeneity of the primary electron beam. Curve III gives the correction due to the same cause applicable to the experiments of Compton and Van Voohris.

in that most of them have nearly the energy corresponding to the applied field, but there is always an appreciable group with variously diminished energies.

It is clearly incorrect, therefore to assume, as did Hughes and Klein, that every electron found in the primary beam has energy corresponding to the accelerating field. It is necessary first to subtract the ineffective group of slow secondaries and then to make a step by step correction to take account of the velocity distribution among the remaining electrons which are able to ionize. These corrections to Hughes and Klein's results may be made to at least the right order of magnitude by use of curve II, Fig. 3. The ordinate at any voltage V_a

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[4] Lehman and Osgood, Proc. Camb. Phil. Soc. **22**, 731 (1925).

is the percentage of Hughes and Klein's value of probability of ionization at voltage $V_a - \delta$ (where δ is the number marked on the curve) which should be added to their value for voltage V_a in order to give a value of this probability at voltage V_a, which is thus corrected for the neglect of the inhomogeneity in the velocities of electrons in the primary beam.

For example, at $V_a = 150$ volts, the correction to Hughes and Klein's probability of ionization, from this cause, is the addition to their value for 150 volts of 46 percent of their value for 150−25 or 125 volts.

Finally, as we suggested in our previous paper, Hughes and Klein neglected the decrease in gas density in the region of ionization caused by the warming of the gas by heat from the filament. In our experiments this amounted to a rise of about 25°C above the temperature of the room. The electrode arrangement of Hughes and Kein would indicate rather greater warming than in our apparatus. As a guess, which is probably fairly accurate, we may take the gas temperature in their experiments to be 60°C, which necessitates an increase of about 12 percent in all their values of probability of ionization.

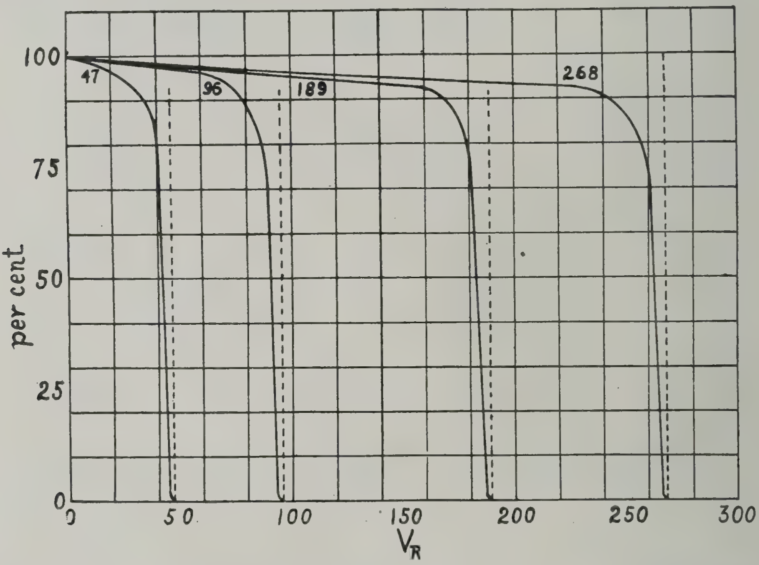

Fig. 4. Curve showing velocity distribution in primary electron beam in experiments of Compton and Van Voorhis.

Thus, to all probabilities reported by Hughes and Klein, should be added three corrections whose values are given approximately as follows: (1) a correction for variation in effective size of grid holes given by Fig. 3, curve I; (2) a correction for secondary electrons and velocity distribution of primary electrons given by curve II; (3) a correction of 12 percent for the warming of the gas by the filament.

Turning now to the values which we previously reported, we may note that the first and third corrections described in the preceding paragraph do not need to be considered, since they were eliminated or allowed for in our original experiments. We did not, however, sufficiently consider the second source of error,—that due to velocity distribution in the primary electron stream. We have, therefore, measured the velocity distributions for various accelerating fields V_a in our original apparatus, with results shown in Fig. 4. The collecting

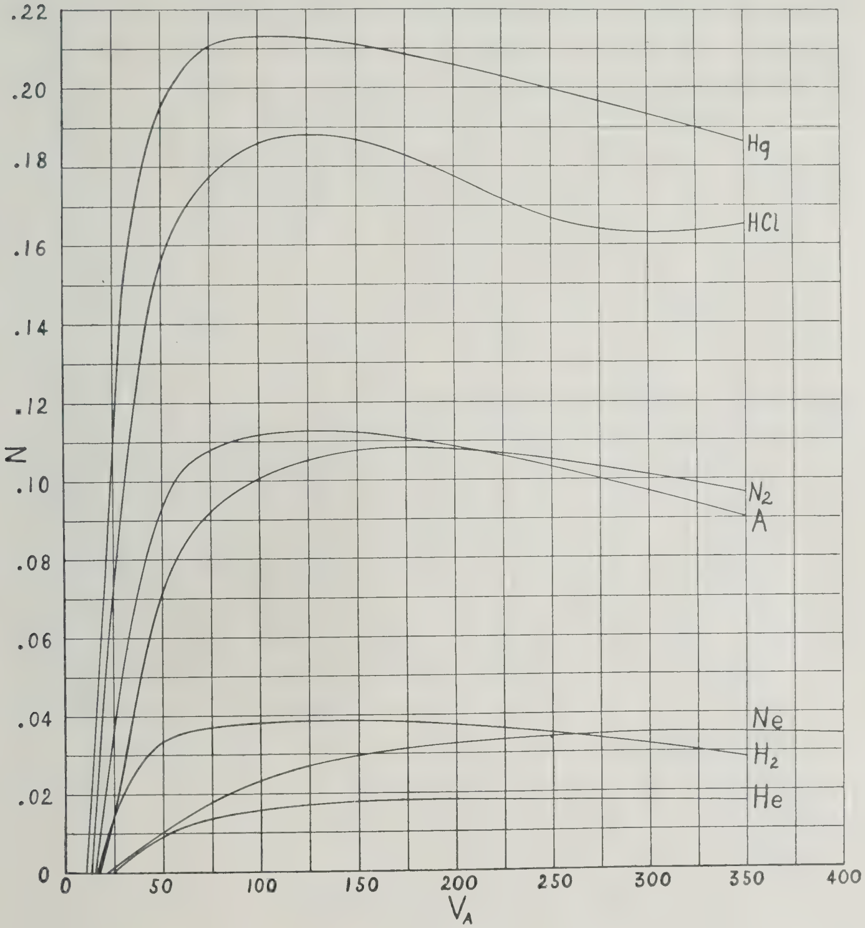

Fig. 5. Curves showing the number N of ionizing collisions made per cm path through gas at 0.01 mm pressure at 25°C.

field V_r held back all secondary electrons, so that we were not subjected to error from the phenomenon described by Lehman and Osgood The lack of homogeneity in our electron stream, however, leads to the necessity of a correction to our previous results of an amount shown in Fig. 3, curve III, which was derived from velocity distribution curves like those in Fig. 4, by the same method employed in obtaining curve II

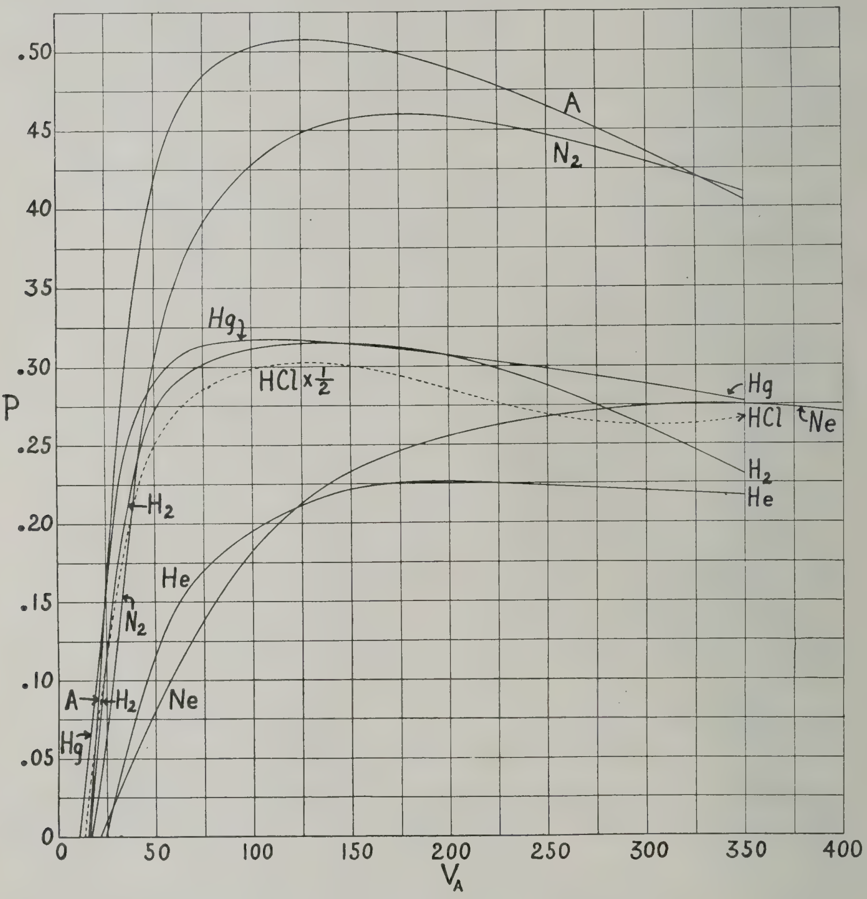

Fig. 6. Curves showing probability of ionization at a collision as a function of the speed of the impacting electron in volts.

for Hughes and Klein's results. Thus, for instance, we must add to our previous value for the ionization by 150 volt electrons, 8.5 percent of our value at 142 volts.

That the values finally arrived at in this way are fairly accurate is indicated by a comparison of our corrected results with the corrected results of Hughes and Klein, as shown in Table I. In view of the magnitude and approximate character of the corrections in the latter case, we believe the agreement is satisfactory.

TABLE I

Comparison of probabilities of ionization from corrected results of Compton and Van Voorhis and of Hughes and Klein.

Va	Helium		Neon		Argon		Hydrogen		Nitrogen	
(volts)	C&VV	H&K	C&VV	H&K	C&VV	H&K	C&VV	H&K	C&VV	H&K
50	.115	.109	.083	.080	.430	.434	.259	.262	.310	.333
100	.197	.155	.181	.183	.500	.496	.310	.286	.425	.457
200	.227	.201	.255	.256	.490	.527	.303	.291	.457	.502
300	.219	.175	.274	.244	.436	.473	.259	.230	.430	.422

In Figs. 5 and 6 we give the final corrected values calculated from our experiments. The values of electronic mean free paths used in calculating the probabilities shown in Fig. 6 are, for 1 mm gas pressure at 25°C, He(0.1259), Ne(0.0787), A(0.045), H_2(0.0817), N_2(0.0425), Hg(0.0149), HCl(0.0322) in cm.

Finally we have made some attempts to reconcile with these results the values reported by Jesse.[3] The complicated geometry of the electric fields, the existence of secondary and perhaps tertiary electron emission and the presence of the exposed insulating walls of the glass vessel have all been shown to introduce complicating effects, so that we have not succeeded in showing how his results may be brought into agreement with the others. Jesse cites evidence to show that his second "maximum" is spurious. Neglecting this, his results are in rough agreement with ours, as was shown in our earlier paper.

PALMER PHYSICAL LABORATORY,
PRINCETON, N. J.
March 1, 1926.

THE IONIZATION OF OXYGEN BY ELECTRON IMPACT AS INTERPRETED BY POSITIVE RAY ANALYSIS

By T. R. Hogness and E. G. Lunn

Abstract

Using an apparatus previously described, in which ions formed by impact of electrons of definite energy are analyzed by Dempster's positive ray method, the relative numbers of 0_1^+ and 0_2^+ are measured at different pressures and electron energies. Over a range of pressure from $<10^{-5}$ to 10^{-2} mm of mercury in pure oxygen, and over a large range of partial pressures of oxygen in mixtures with helium and with argon, the ratio $0_2^+/0_1^+$ remains practically constant. Evidence is thus given that 0_2^+ and 0_1^+ are formed by independent primary processes and, therefore, that an impact electron of sufficient energy can either ionize the molecule and form 0_2^+ or dissociate the molecule forming 0_1^+. The ionization potentials were determined: $0_2=0_2^++\epsilon$; 13 volts and $0_2=0_1^++0+\epsilon$; 20 volts. The latter, together with the ionizing potential of atomic oxygen, gives 6.5 volts (150,000 cal. per mol) for the heat of dissociation of oxygen. Both molecular and atomic negative ions were found. The above results are correlated with band-spectra data, with the recent theory of Franck on dissociation by absorption of radiation, and with the structure of the oxygen molecule.

THE following paper discusses experiments on oxygen made with the previously described[1,2,3] method for the positive ray analysis of the products of electron impact ionization in gases.

Experimental Details

The apparatus was that previously employed, except that the slits were narrowed to permit the use of higher pressures in the ionization tube, and to increase the resolving power. The increased resolving power was necessitated by the impossibility of freeing the oxide-coated platinum filament from all traces of residual gases, and the consequent appearance of peaks due to these impurities; these peaks, though small, would, with lower resolution, merge into the oxygen peaks and vitiate the measurements of their intensity. The ions of these impurities are presumed, from their specific charges, to be: Hg^+, CaO^+, CO_2^+, $30=?$, $29=?$, N_2^+, $20=?$, $19=?$, H_2O^+, OH^+, O^+, $15=?$, N^+ and C^+. With the slits narrowed to 0.28 mm these peaks are sharp and well separated. The mercury peak disappears after liquid air has been on the traps for some days, while the other peaks either disappear or become negligibly small after prolonged heating of the filament. Judging from the peak intensities obtained in previous work with very low pressures of hydrogen[2] and nitrogen,[3] the partial pressures of the above impurities were $<10^{-6}$ mm of mercury, except in those experiments in which the highest filament temperatures were employed.

The oxygen was prepared by electrolysis of aqueous barium hydroxide and was dried with phosphorus pentoxide. Before entering the ionization tube it passed through a liquid air trap.

Positive ions. As shown by the figure, the relative intensity of the ions O_1^+ and O_2^+, as measured by the ratio of the peak intensities, remains practically constant over a range of pressure from $<10^{-5}$ to 10^{-2} millimeters of mercury. Evidence is thus given that O_1^+ and O_2^+ are formed by independent processes, and hence that an impact electron of sufficient velocity can either produce an O_2^+ ion which does not dissociate on collision with gas molecules:

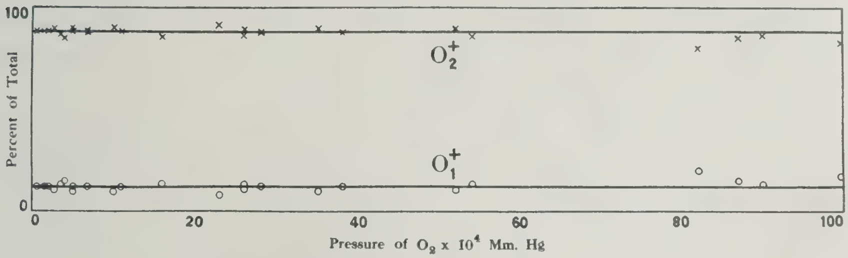

Fig. 1. Precentage of 0_1^+ and 0_2^+ as a function of pressure.

$$O_2=O_2^++\epsilon\ , \tag{1}$$

or it can dissociate the molecule and ionize one atom as the primary process:

$$O_2=O_1^++O+\epsilon\ . \tag{2}$$

The slight increase in the percentage of O_1^+ at the higher pressures is probably due to the formation of these ions from the impurities, for, owing to a specific inhibiting effect of oxygen on the emission of electrons from an oxide-coated filament,[4] it was necessary to raise the filament to a high temperature and hence to increase the concentration of those foreign gases which, on ionization, produce O_1^+-ions.

The relative intensities of O_1^+ and O_2^+ were found to be nearly independent of other experimental conditions, such as the partial

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[1] Hogness and Lunn, Proc. Nat. Acad. Sci. **10**, 398 (1924).
[2] Hogness and Lunn, Phys. Rev. **26**, 44 (1925).
[3] Hogness and Lunn, Phys. Rev. **26**, 786 (1925).
[4] Koller, Phys. Rev. **25**, 671 (1925).

pressure of oxygen in mixtures with helium and with argon, and the speed of the positive ions in the ionization chamber.

In mixtures of oxygen with helium and with argon the percentage of O_1^+ was found to be only slightly larger than in pure oxygen, and this slight increase is probably caused by O_1^+ ions from the impurities due to the high filament temperature made necessary by the small partial pressure of the oxygen. With argon in the tube, peaks of specific charges 40 and 36 (referred to $0=16$) appeared, thus confirming Aston's[5] evidence on the isotopy of argon.

The relative intensities of O_1^+ and O_2^+ are practically independent of the energy of the impact electron from 50 to 200 volts; above 200 and up to 600 volts, increasing this energy gradually decreases the percentage of O_1^+. Similarly, varying the speed of the positive ions in the ionization chamber by changing the field V_3 from 0 to 31 volts does not change the intensity ratio appreciably.

Ionization potentials. The ionization potentials for the formation of O_2^+ and O_1^+ were determined by comparing their disappearing potentials with that of helium in essentially the manner previously described.[2] Oxygen was mixed with helium in the reservoir until the "saturation" intensities of He^+ and O_2^+ were the same, and the disappearing potentials compared; the concentration of oxygen was then increased until the He^+ and O_1^+ "saturation" intensities were equal, and the disappearing potentials of these ions were then measured. Taking 24.5 volts as the ionization potential of helium,[6] the mean of six determinations gave 13 volts as the ionization potential for the formation of O_2^+ and 20 volts for the formation of O_1^+.

Negative ions. On reversing the magnetic field and the electrical fields V_3 and V_4, the negative ions O_2^- and O_1^- were observed. These had previously been found by J. J. Thomson.[7] The atomic ion was the more intense under all conditions studied; but the intensities of both O_1^- and O_2^- were so small as to preclude the possibility of their formation being related to the positive ion process.

DISCUSSION

The ionization of oxygen has been studied by McHenry[8] and by Smyth.[9] McHenry used Thomson's positive-ray apparatus and hence experimental conditions that make difficult any comparison of his results with those above. The present results differ somewhat from those of Smyth. His published curves show a larger percentage of O_1^+ than was found above; this is perhaps due to the presence of N_1^+ and other impurities not resolved by his apparatus. The ion of apparent $m/e=8$, which Smyth observed, was probably not O^{++}. In the present work its peak appeared as a very broad one of small height—indicative of formation by some secondary process, such as the disruption of an O_2^+-ion which had fallen through the full analyzing field.[10] The above experiments show no evidence of the discontinuity in the ionization curves at 450 volts found by Smyth. His measurements gave 15.5 and 23.0 volts as the ionization potentials. We believe Smyth's values for these ionization potentials to be in error, owing, perhaps, to incorrect initial velocity corrections; but their difference $(23.0-15.5=7.5$ volts) agrees well with that (7 volts) found above.

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[5] Aston, Phil. Mag. **39,** 611 (1920).

[6] Lyman, Science **56,** 167 (1922).

[7] J. J. Thomson, Rays of Positive Electricity, p. 71.

[8] McHenry, Phil. Mag. **45,** 433 (1923).

[9] Smyth, Proc. Roy. Soc. **105 A,** 116 (1924).

Of the several determinations of the ionizing potentials of oxygen[11] only that of Mackay[12] shows ionization as low as 13 volts; he found two potentials at 12.5 and 16.1 volts. Studying low voltage arcs in oxygen, Lockrow and Duffendack[13] found critical potentials at 16.1 and 19.5 volts. The lower, that at which the arc broke, they ascribed to the formation of O_2^+; the upper, a critical potential for changes in the spectrum, was attributed to the formation of O_1^+ by the process $O_2=O_1^++O+\epsilon$. The lower potential of Mackay and the upper one of Lockrow and Duffendack are thus in good agreement with those found above for the formation of O_2^+ and of O_1^+ respectively.

From the evidence based on the magnetic and chemical properties of oxygen, G. N. Lewis[14] has given $:\underset{\cdot}{\ddot{\mathrm{O}}}:\,:\underset{\cdot}{\ddot{\mathrm{O}}}:$ as the schematic structure of the oxygen molecule—a molecule then with two unpaired electrons. Now Saunders[15] has pointed out that atoms with unpaired electrons have low ionizing potentials, the tendency of electrons to pair resulting then in the observed alternation in the value of the ionization potentials of the elements with increase in atomic number; Mulliken[16] and Birge[17] have suggested an analogy between the energy levels of atoms and of molecules. It might therefore be anticipated that, because of the two unpaired electrons in the oxygen molecule, the ionization potential of oxygen would be lower than that of nitrogen. Experiment shows this to be the case. It might be expected, too, that oxygen, containing, as it does, three distinct kinds of electrons (bonding, unpaired—non-bonding, and paired—non-bonding) would have two ionization potentials in addition to that for the disruption of the molecule. Now Mackay[12] did find two lower ionization potentials. From this point of view the lower one (12.5 volts) perhaps corresponds to the ejection of an unpaired electron, the upper one (16.1 volts) to the ejection of a paired—non-bonding electron.*

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[10] See Smyth, Phys. Rev. **25,** 452 (1925).

[11] For a summary of these see Compton and Mohler, Bull. Nat. Res. Council, vol. 9, part 1, *Critical Potentials.*

[12] Mackay, Phys. Rev. **24,** 319 (1924).

[13] Lockrow and Duffendack, Phys. Rev. **25,** 110 (1925).

[14] G. N. Lewis, Chemical Reviews **1,** 231 (1924); J. Am. Chem. Soc. **46,** 2027 (1924).

[15] Saunders, Science **59,** 47 (1924).

[16] Mulliken, Phys. Rev. **26,** 561 (1925).

[17] Birge, Nature **117,** 300 (1926).

The difference in the processes by which the atomic ions are formed in the ionization of oxygen and of nitrogen suggests correlating these processes with the recent theory of Franck[18] on the dissociation of molecules by the absorption of radiation. Franck assumes that the absorption of a light-quantum results only in an electron transition and that the nuclear separation remains unchanged at the moment of this transition. With the electron in a new energy level the nuclei then find themselves held together by a different binding energy; this different binding energy gives rise to a different amplitude and hence, a different frequency of vibration. He further assumes that there is a limiting distance of approach of the nuclei, beyond which there will be sufficient repulsion to cause disruption, and as the binding force is weakened, i. e., as the equilibrium positions of the nuclei are more widely separated, this limiting distance of approach becomes greater. If then, as the result of an electron transition, the equilibrium positions of the nuclei are suddenly at a greater distance apart than before, the two nuclei may, at the moment of transition, be beyond the limiting distance of approach and hence disruption will follow. Dymond[19] found this to be the case in iodine, and Birge and Sponer[20] have recently found this to be true of oxygen as well. Professor Birge has informed us that ionized oxygen in the excited state corresponding to about 20 volts energy has a much slower vibration frequency than the normal state; this means that the equilibrium positions are at greater nuclear separation. Very probably then, the mechanism assumed by Franck for dissociation by absorption of radiation and by electron impact applies to this case of dissociation. Nitrogen does not show this same difference in vibration frequencies in the normal and ionized states, so that the nitrogen nuclei would not be beyond the limit of closest approach in the N_2^+ ion produced at 24 volts[3] and no spontaneous dissociation would follow.

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* The O_2^+ (20 volts) which spontaneously breaks down into O and O^+ may be regarded as being either an O_2^+ with a remaining electron excited, or an O_2^+ with a different kind of electron (bonding) removed from that produced at 13 volts. In our work on nitrogen[3] the latter view was assumed, while Sponer has since suggested the former. The evidence favoring Dr. Sponer's suggestion is that but one series limit for the electron levels in nitrogen is known. Naturwiss. **13,** 275 (1926).

[18] J. Franck, Trans. Faraday Soc., 1925.

[19] Dymond, Zeits. f. Physik **34,** 553 (1925).

[20] Birge and Sponer Abst. 13, Stanford Meeting; Birge, Abst. 14, *ibid.*; Birge and Sponer (to be published in full).

It may be recalled that in the case of hydrogen[2] and nitrogen[3] the measurement of the ionization potentials for the formation of H_1^+ and N_1^+ respectively could give only upper limits to the heats of dissociation as the atomic ions are formed by secondary processes. In the case of oxygen, however, since O_2^+ is formed by a direct process, the heat of dissociation of oxygen can be calculated unambiguously. For

$$O_2 = O_1^+ + O + \epsilon;\ 20\text{ volts} \tag{3}$$
$$O = O_1^+ + \epsilon\ ;\ 13.5\text{ volts}^{21} \tag{4}$$

which, by subtraction, gives 6.5 volts or 150,000 calories per mol as the heat of dissociation of oxygen. The possible limits for the heat of dissociation of oxygen as set by critical potential measurements have been discussed by Wulf. [22] Owing to a lack of interpretation of those measurements the limits were rather wide—56,400 and 137,400 cal. per mol. The latter agrees within the experimental error with that found above, and the new limits are set by the limits of accuracy of the determination of the ionization potential. No claim is made for great accuracy in the above critical potential measurements. As previously done we might make a conservative estimate of ±1 volt, although the maximum deviation of our few values from the above means was 0.4 volt. Born and Gerlach,[23] following a suggestion of Franck and Grotrian, and utilizing Warburg's[24] measurement of the long wave-length limit for the formation of ozone, have calculated the heat of dissociation of oxygen to be 162,000 cal. per mol. Since we obtained our value of 6.5 volts, Birge and Sponer have calculated the heat of dissociation from data derived from band-spectra. The concordance of their value of 7.05 ± 0.03 volts (162,600 ± 700 cal.) with those of two such very different experimental methods suggests strongly

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[21] Hopfield, Phys. Rev. **21,** 710 (1923).

[22] Wulf, J. Am. Chem. Soc. **47,** 1944 (1925).

[23] Born and Gerlach, Zeits. f. Physik **5,** 433 (1921).

[24] Warburg, Sitzungsber. d. preus. Akad. d. Wiss., Math-phys. Kl. 1914, p. 872.

the fundamental correctness of the assumptions underlying these methods.

Throughout the above paper it has been tacitly assumed that the ion of $m/e=16$ was O_1^+ and not O_2^{++}. It is now seen that the chief justification for this assumption is that it is consistent with the spectroscopic observations of Lockrow and Duffendack,[13] and that it leads to a consistent value for the heat of dissociation of oxygen. Professor Birge has sufficient data to assure us that the energy of formation of O_2^{++} is greater than 20 volts. The ion appearing at 20 volts can therefore be only O_1^+.

In conclusion, the authors wish to express their thanks to Prof. R. T. Birge and Dr. H. Sponer of the Department of Physics for making available a large amount of unpublished results, as well as for their kindly interest in the progress of this work.

Department of Chemistry,
University of California,
March 23, 1926.

JUNE, 1926 PHYSICAL REVIEW VOLUME 27

ANALYSIS OF POSITIVE IONS EMITTED BY A NEW SOURCE

By Henry A. Barton,* Gaylord P. Harnwell, and C. H. Kunsman.

Abstract

Certain iron oxide crystals containing about one percent of some alkali metal or alkaline earth have been developed by the Fixed Nitrogen Research Laboratory for use as catalysts in the synthesis of ammonia. It has been found that these substances also have great experimental utility as constant and abundant emitters of positive ions. The writers have tested various methods of mounting and heating these emitters. They have also analyzed their emission by the use of a mass spectrograph which has been described by Smyth. Separate catalyst samples containing respectively Na, K, Rb, Cs, Mg, Ca, and in one case both Ba and Sr have been shown in this way to emit only the corresponding singly charged positive ion. No doubly charged ions were observed, nor any ions of the other elements composing the catalysts. The alkali metal ions were emitted at lower temperatures than the alkaline earth ions. Particularly in the case of the latter, a preliminary treatment consisting of reduction at red heat in an atmosphere of hydrogen increased the emission.

Emission from hot platinum was also observed consisting of Na^+ and K^+ ions. This was a surface effect and diminished rapidly with time.

Introduction

Kunsman[1] has described a new and convenient source of positive ions which is finding many uses in experimental research. This source consists of heated crystal granules of certain catalysts developed for the synthesis of ammonia at the Fixed Nitrogen Research Laboratory in Washington. Briefly, these consist of a fused mixture of iron oxide and about one percent of an oxide of an alkali metal or alkaline earth, with sometimes the addition of about one percent of aluminium oxide. The method of preparation[2] and an x-ray analysis[3] of the crystals have recently been published.

When the crystals are heated they emit positive ions in large numbers. If they are further prepared by reduction in an atmosphere of hydrogen and then glowed and degassed in a good vacuum, the positive ion current is quite constant. This current in a high vacuum is a function of temperature and accurately obeys Richardson's equation, $I=AT^{1/2}\epsilon^{-b/T}$ for thermionic emission. More recently Kunsman has considerably extended his investigation of the thermionic properties.[4]

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* National Research Fellow, Harvard University.

[1] Kunsman, Science, **62**, 269 (1925).

[2] Larson and Richardson, J. of Ind. Chem. **17**, 971 (1925).

[3] Wyckoff and Crittenden, J. Am. Chem. Soc. **47**, 2866 (1925).

For precise experimental work using this type of positive ion source, it is, of course, highly important to have full knowledge of the nature and homogeneity of the ions emitted. The present paper describes a positive ray analysis undertaken primarily to answer this question. Seven samples were investigated, being iron oxide crystals as described, and containing, respectively, caesium, rubidium, potassium, sodium, magnesium, calcium, and, in one sample, both barium and strontium.

APPARATUS

The experimental arrangement[5] is shown schematically in Fig. 1. Some of the sample source under investigation was mounted on a platinum filament at *F*, this being supported by the leads (not shown) which carried the heating current. The arrangement of slits, electric and magnetic fields is obvious. *P* was connected to a Compton electrometer. A mass spectrum was obtained by progressively varying *V* with *H* constant and observing the electrometer current. In most of the experiments the field strength was about 4400 gauss and *V* was varied from 0 to 400 volts. S_2 and S_3 were 6 cm apart. A vacuum of better than 10^{-4} mm of Hg was maintained throughout. The best resolution obtained was not sufficient to separate isotopes, but easily distinguished ions of elements in different rows of the periodic table.[6]

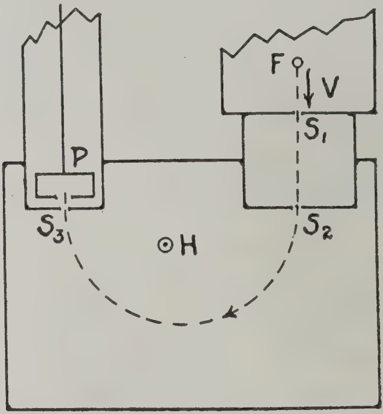

Fig. 1. Apparatus.

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[4] Kunsman, to be published shortly.

[5] The tube used was that described by Smyth, Phys. Rev. **25**, 452 (1925), except that two of the electrodes were removed and the evacuating arrangements simplified.

[6] In two runs the potassium peak indicated by its shape that little more resolving power would have been needed to separate the two isotopes at 39 and 41.

In the course of the experiments four different methods of mounting and heating the catalysts were used. At first the tube was so oriented that the filament and slit S_1 were in the same horizontal plane, a trough with an open side towards S_1 could be used. Later the arrangement was changed so that F was above S_1 as shown in Fig. 1. It was then necessary to turn the trough open side up so as not to spill out the granules and provide small perforations in the bottom for the emission. This method proved less satisfactory, so a narrow, twisted strip of platinum was next mounted and covered as completely as possible with a coating of pulverized catalyst granules. The coating was put on with the aid of paraffin as a vehicle in the same manner as is frequently used in the preparation of oxide coated filaments, the paraffin being vaporized by heating, once the active material is in place. This method has the valuable advantage of providing a large emitting surface.

Although the last mentioned method proved very satisfactory for the alkali metal catalysts, a fourth type of filament was used for those containing alkaline earths. Difficulty was found in coating strip filaments with these. They did not seem to adhere as well as the alkali metal samples. This resulted in an uneven coating so that the heating along the filament was not uniform. Owing to the greater temperatures which had to be used to obtain emission in these cases, this difficulty shortened the life of the filaments considerably. The type of filament finally adopted consisted of a thin-walled platinum tube with small perforations in the side toward S_1 to allow ion emission. This was filled with a finely granulated sample of catalyst and the ends squeezed together to keep it in. The alkaline earth and rubidium samples were investigated in this way.

All of the filaments were less than 1 cm in length. They required heating currents ranging from 4 or 5 amps. for the twisted strip type to 15 amps. for the tube type.

Alkali Metals

Mass spectra of the emission from the four alkali metal samples are given in Fig. 2. The ordinates, representing electrometer current, are arbitrary and not comparable from one curve to another. This arises from the fact that the electrometer current depended upon the pressure of gas in the path of the ions (which caused scattering), the effective area of the granules mounted on the filament, and the exact position of the latter. It was not possible to have these always the same.

Furthermore no means were available for measuring the temperature of the filament.

Caesium (*132.8*). The mass spectrum of the caesium sample shows a large diffuse peak corresponding to Cs^+ ions. The resolution of the apparatus is not as good for heavy ions as for light, which chiefly accounts for the width of this peak. It is also characteristic of the apparatus that the peak shades off toward lower m/e values. It is quite possible, however, that the shoulder just above 80 is due to Rb^+ impurity. The curve was extended below 50 and very large K^+ and Na^+ peaks observed. These have not been indicated in the figure because it was later definitely established that they came from the platinum filament itself or from a contamination on it from previous samples. Later a new filament was prepared and tested for K^+ and Na^+ before being coated. After this had been coated with some of the caesium sample, a large Cs^+ peak was obtained with little or no K^+ or Na^+.

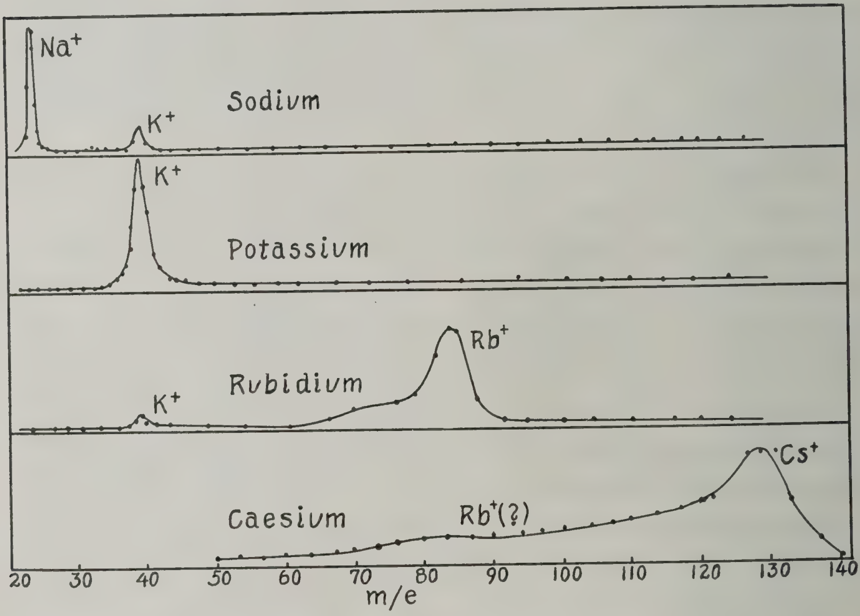

Fig. 2. Mass spectra of catalysts containing alkali metals.

Rubidium (*85.5*). The emission from this sample was at first small. After reduction by the same method as will be described in connection with the alkaline earth samples it was much better. The curve in Fig. 2 shows a run then taken, the only impurity being a small amount of K^+.

Potassium (*39.1*). The curve shows remarkable freedom from the other alkali metals as impurities.[7]

Sodium (*23.0*). The curve of this sample shows a very sharp principal peak indicative of the resolution obtainable at the lower end of the m/e scale. The K impurity was much more pronounced when the filament was first heated, then diminished rapidly and was still diminishing when the curve was taken. It was probably due chiefly to emission from the platinum, of which more will be said below. In the portion of the m/e scale through which a broken line has been drawn, rates of electrometer deflection were not timed. They were observed carefully, however, and it may be said definitely that no peaks comparable with the K^+ peak were to be found.

ALKALINE EARTHS

Mass spectra obtained from the catalysts containing the alkaline earths are shown in Fig. 3. As mentioned above, it was found necessary to go to higher temperatures to obtain characteristic positive ion emission from these substances. Also the emission was greatly increased if they were submitted to a preliminary period of reduction. This was done by mounting the filament in an atmosphere of hydrogen at about 1 cm pressure and heating at a redness just above visibility for about 24 hours. It is possible that the continued heating altered the condition of the sample as well as reducing the surface. Samples so prepared were found to emit singly charged positive ions of the alkaline earths, but in almost all of the runs, certain impurities of sodium and potassium were found which never completely disappeared with time.

In Fig. 3 two characteristic curves are plotted for each sample. The curve marked I represents one of the first runs, which was taken at a low temperature. The procedure then was to increase the temperature and, after a certain lapse of time, to allow conditions to reach a possible state of equilibrium, another run was taken. This process was continued until the filament burned out or the leads became dangerously hot. The curve marked II is a representative run taken at the highest temperature obtainable. The comparative temperatures were judged entirely by the current passing through the filament. The time elaspsing between runs I and II varied with the samples but was of the order of several hours. The impurities were found to decay very rapidly with time, probably exponentially. The ordinates of the curves of the different substances are again not comparable because the conditions, particularly the temperatures, were not identical.

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[7] This curve was taken some months before the rest of the work was done. It was mentioned by Kunsman. (Ref. 1.)

Barium (137.37) and Strontium (87.63). Curve I shows no evidence of anything but Na^+ and K^+ which were evidently present as impurities, probably, to a very large extent, coming only from the platinum. Curve II shows a very small peak at K^+, a distinct but very broad peak at Sr^+, and a very large peak at Ba^+. The Sr^+ peak is surprisingly small relative to the Ba^+ peak, the reason for this being uncertain. No evidence of Sr^{++} or Ba^{++} was found.

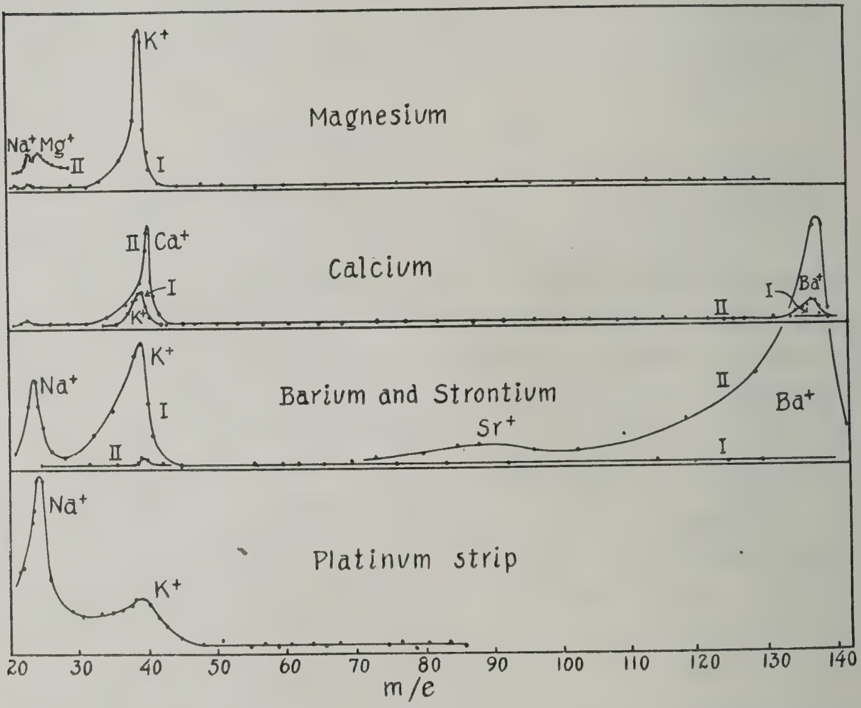

Fig. 3. Mass spectra of catalysts containing alkaline earths and of bare platinum.

Calcium (40.07). Curve I shows only a K^+ peak. Curve II shows a very slight Na^+ peak, a large peak for Ca^+ and a peak of about one-third the height of Ca^+, for Ba^+. An incomplete run at a slightly higher temperature was obtained in which the Ba^+ peak rose relatively to the Ca^+ peak. Again no evidence of Ca^{++} or Ba^{++} was obtained.

The rather small shift of the principal peak toward higher *m/e* in passing from low to high temperatures is perhaps not sufficient in itself to justify the statement that the K^+ emission is replaced by Ca^+. There is good reason to believe, however, that this shift is genuine.

Furthermore, other evidence is quite in favor of the existence of Ca^+ emission. For example, this 'shifted' peak remained approximately constant at any given temperature, whereas in all cases where K^+ was present as an impurity, the peak corresponding to it diminished rapidly with time. These facts together with the undoubted emission of the other alkaline earths are considered conclusive evidence for the existence of Ca^+ emission.

Magnesium (*24.32*). Curve I shows a small Na^+ peak and a very large K^+ peak. In the following runs the K^+ fell in comparison with the Na^+ peak and they both dropped off with time at constant temperature. In the run at the highest temperature obtained the Na^+ and Mg^+ peaks were distinctly resolved. The filament burned out before the region containing the K^+ peak could be examined. In subsequent runs the filament never lasted long enough at a temperature sufficient to produce Mg^+ to examine in detail the other regions, but no evidence of anything but a K^+ peak was discovered. Voltages high enough to cover the region where Mg^{++} would lie were not used.

IONS FROM PLATINUM

The first few runs with the potassium sample of catalyst showed sodium ions also present. Subsequent runs using the same filament charged with caesium catalyst showed sodium and potassium in addition to caesium ions. The filament was taken out and chemically cleaned. It was then replaced and found to emit sodium and potassium ions as before but the caesium had been quite removed. The filament was taken out a second time and heated white hot in a blast flame to volatilize any traces of alkali metals left on the surface by the catalyst samples. In spite of this the sodium and potassium ions still persisted. A new platinum strip was then mounted and this too was found to emit sodium and potassium ions. The first curve obtained in this case is given in Fig. 3.

No particular study was made of this emission of ions by the platinum itself. It was observed however that an increase in the temperature of the strip always produced increased ion emission, particularly of potassium, and that this very quickly diminished if the temperature were then kept constant. It was partly due to the latter fact and partly to care in covering up as much of the platinum surface as possible with catalyst that the sodium, potassium, and rubidium curves show little evidence of this emission.

More extended investigations of the emission from hot platinum have been made by others. A summary of these investigations, together with certain conclusions drawn from the results, has been given by Richardson.[8] The above observations, as far as they go, confirm these conclusions. This is particularly the case as regards the constitution of the ions emitted by platinum, for the present resolving power appears to be better than that of any apparatus heretofore used to study the phenomenon.

DISCUSSION

The mass spectra given in Figs. 2 and 3, together with the circumstances of their production, lead to the conclusion that the only ions emitted in each case were those of the alkali metal or alkaline earth present in the catalyst. The much more abundant iron and oxygen atoms did not appear as ions, nor did aluminium in the catalysts where it too was present. It is interesting that the alkaline earth ions, like those of the alkali metals, were only singly charged, in spite of their possession of two loosely bound valence electrons.

The evidence does not give sufficient basis for much discussion of the mechanism of emission. Very roughly it appeared in the case of the alkaline earths that the lighter elements required higher temperatures to produce emission. Certainly these elements required considerably higher temperatures than the alkali metals. The difficulty seems to vary in the same direction as the ionizing potentials. This may account for the difference in the heights of the barium and strontium peaks.

The chief distinction between these emitters and others is, of course, their constancy and relative inexhaustibility. There is evidently something about their structure which permits the ion-forming atoms to diffuse readily and abundantly to the surface. In most other cases the ion emission rapidly falls off as the supply or at near the surface becomes exhausted.[8]

The authors are indebted to members of the staff of the Fixed Nitrogen Research Laboratory and also to Professors K. T. Compton and H. D. Smyth for valuable suggestions and indispensable assistance.

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January 29, 1926.

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[8] Richardson, The Emission of Electricity from Hot Bodies, Chaps. VI and VII.

ON THE THEORY OF ELECTROSTATIC ALTERNATORS

BY A. W. SIMON[1]

ABSTRACT

A more elegant method than that previously given for the solution of the equations involved in the theory of electrostatic alternators is given, and illustrated by application to an electrostatic alternator of eight inductors and eight carriers, in which each carrier as it comes in front of an inductor is connected to the next following inductor by means of a brush and insulated arm. The method can be extended to the solution of electrostatic alternators of m carriers and m inductors, where each carrier is connected to the inductor next following, also where each carrier is connected by means of brushes properly placed to the pth inductor following. It may also be applied to electrostatic alternators with m inductors and $2m$, $3m$, or $4m$ carriers, and to electrostatic alternators of the Wimshurst type. With regard to the eight inductor alternator it is shown that three waves travel around the machine with periods corresponding to the time of 2 revolutions, 1 revolution, and 2/3 revolutions. The amplitude factor for each wave per eighth revolution is calculated approximately. Finally the effect of the initial conditions (potentials) on the action of the machine is discussed. It is shown that the potentials of the inductors of the machine eventually lag $\pi/4$ behind each other.

THE quantitative theory of a four inductor alternator of the type to be discussed in the present work has already been given,[2] and a general method of solution of alternators of this type outlined.[3] Since the publication of this work, however, it has been possible to develop a much more elegant method of solving the equations involved in the theory of these machines, and our present work is concerned both with an exposition of this method as well as a discussion of the physical interpretation of the results obtained by its application.

As the subject of our analysis we shall take an eight inductor electrostatic alternator, and present the theory of this machine in a form which admits of ready extension to alternators of this type with any number of inductors.

The machine studied is represented diagrammatically in Fig. 1. It consists of eight fixed inductors, and eight revolving carriers, and operates in a manner easily seen from the figure. The inductors are assumed to be identical in shape and symmetrically mounted, and the same is assumed to apply to the carriers.

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[1] National Research Fellow.

[2] A. W. Simon, Phys. Rev. **25**, 368 (1925).

[3] A. W. Simon, Phys. Rev. **26**, 111 (1925).

By exactly the same method as was employed in the case of the four inductor alternator already cited,[4] it can be shown that the potentials of the inductors after $(n+1)$ and n cycles satisfy a set of equations of which the left members take the form:

$$\begin{array}{llllllllllllllll}
a & V_0(n+1) & +h & V_1(n+1) & +g & V_2(n+1) & +f & V_3(n+1) & +e & V_4(n+1) & +d & V_5(n+1) & +c & V_6(n+1) & +b & V_7(n+1) \\
b & \text{``} & +a & \text{``} & +h & \text{``} & +g & \text{``} & +f & \text{``} & +e & \text{``} & +d & \text{``} & +c & \text{``} \\
c & \text{``} & +b & \text{``} & +a & \text{``} & +h & \text{``} & +g & \text{``} & +f & \text{``} & +e & \text{``} & +d & \text{``} \\
d & \text{``} & +c & \text{``} & +b & \text{``} & +a & \text{``} & +h & \text{``} & +g & \text{``} & +f & \text{``} & +e & \text{``} \\
e & \text{``} & +d & \text{``} & +c & \text{``} & +b & \text{``} & +a & \text{``} & +h & \text{``} & +g & \text{``} & +f & \text{``} \\
f & \text{``} & +e & \text{``} & +d & \text{``} & +c & \text{``} & +b & \text{``} & +a & \text{``} & +h & \text{``} & +g & \text{``} \\
g & \text{``} & +f & \text{``} & +e & \text{``} & +d & \text{``} & +c & \text{``} & +b & \text{``} & +a & \text{``} & +h & \text{``} \\
h & \text{``} & +g & \text{``} & +f & \text{``} & +e & \text{``} & +d & \text{``} & +c & \text{``} & +b & \text{``} & +a & \text{``}
\end{array}$$

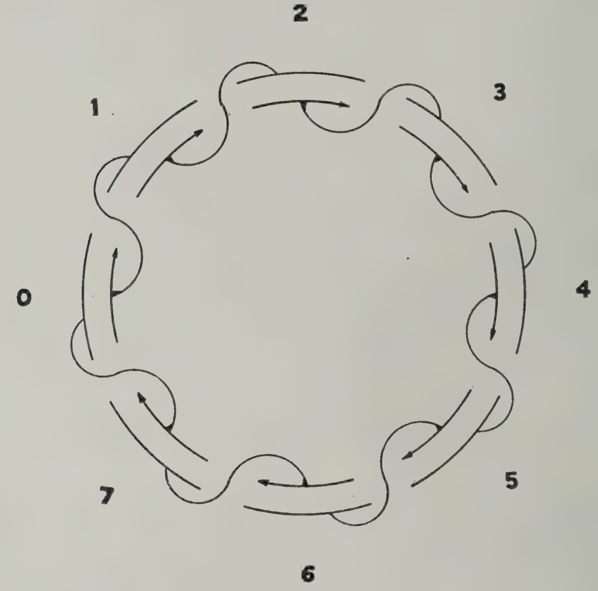

Fig. 1. An eight inductor electrostatic alternator.

and the right members take exactly the same form except that the coefficients a, b, c, etc. are replaced by a', b', c', etc. respectively, and the argument $(n+1)$ of the functions $V_s(n+1)$ is replaced by n.

I. General Solution of the Voltage Equations

Of fundamental importance for the mathematical solution of these equations is the following matrix, in which ω_j stands for the eighth root of unity corresponding to the amplitude of $j2\pi/8$.

$$\begin{array}{cccccccc}
\omega_0^0 & \omega_0^1 & \omega_0^2 & \omega_0^3 & \omega_0^4 & \omega_0^5 & \omega_0^6 & \omega_0^7 \\
\omega_1^0 & \omega_1^1 & \omega_1^2 & \omega_1^3 & \omega_1^4 & \omega_1^5 & \omega_1^6 & \omega_1^7 \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\omega_7^0 & \omega_7^1 & \omega_7^2 & \omega_7^3 & \omega_7^4 & \omega_7^5 & \omega_7^6 & \omega_7^7
\end{array} \qquad (2)$$

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[4] A. W. Simon, Phys. Rev. **24**, 690 (1924).

For the purpose of the following work we shall number the rows and columns from 0 to 7, instead of from 1 to 8, as is the usual custom.

If we multiply the equations in order by the elements in the jth row of this matrix, and add, we obtain an equation of the form:

$$\begin{gathered}[a\omega_j^0+b\omega_j^1+c\omega_j^2+\cdots+h\omega_j^7][\omega_j^0V_0(n+1)+\omega_j^1V_1(n+1)+\cdots]=\\ [a'\omega_j^0+b'\omega_j^1+c'\omega_j^2+\cdots+h'\omega_j^7][\omega_j^0V_0(n)+\omega_j^1V_1(n)+\cdots]\end{gathered}$$

the solution of which is obviously:

$$[\omega_j^0V_0(n)+\omega_j^1V_1(n)+\cdots]=\frac{[a'\omega_j^0+b'\omega_j^1+\cdots]^n}{[a\omega_j^0+b\omega_j^1+\cdots]^n}[\omega_j^0V_0(0)+\omega_j^1V_1(0)+\cdots] \tag{3}$$

and, if we do this for every row, (i. e., if we let j run through the sequence of values 0, 1, $\cdots$ 7) we obtain eight simultaneous linear equations, the left members of which involve the functions $V_s(n)$ and the ω's, and in which the matrix of the coefficients of the left members is exactly the matrix (2). By elimination from this set we can then obtain each of the functions $V_s(n)$ in terms of the quantities $V_s(0)$ and the quantities $[a'\omega_j^0+b'\omega_j^1+\cdots]^n/[a\omega_j^0+b\omega_j^1+\cdots]^n$.

Now the matrix (2) has two important properties which allow us to carry out the process of elimination very easily. (1) If we examine the sum of the quantities in any column, we note that it is the sum of like powers of the roots of the algebraic equation $x^8-1=0$, and from the formula for the sum of like powers of the roots of an algebraic equation, it follows directly that the sum of the quantities in every column of the matrix (or row, if we replace every element of the form of $\omega_p{}^q$ by $\omega_q{}^p$), except the first, is zero. (2) If we divide each row through by the factor which will make the elements in the sth column all unity, the resulting matrix can be obtained from the matrix (2) by s cyclic permutations of the columns of the matrix (2), and has the property that the sum of the coefficients in every column except the sth is zero.

To solve for any $V_s(n)$ then we have merely to divide the equations (3) through by such factors as will make the elements in the sth column of the matrix (2) all equal to unity, and then add the resulting equations.

Accordingly, we have as the general formula for $V_s(n)$:

$$8V_s(n)=\sum_{j=0}^{7}\frac{[\omega_j^0V_0(0)+\omega_j^1V_1(0)+\cdots][a'\omega_j^0+b'\omega_j^1+\cdots]^n/\omega_{sj}}{[a\omega_j^0+b\omega_j^1+\cdots]^n} \tag{4}$$

where ω_{sj} is the element in the sth column and jth row of the matrix (2).

Now while each term of this sum is complex, the sum itself is real, for we can group the complex terms into pairs of conjugate terms, such that the imaginary parts will cancel out in the sum.

This is readily seen from the matrix (2) if in addition we note that each of the expressions in brackets in formula (4) is obtained by combining a sequence of eight quantities, (namely the sequences $V_0(0)$, $V_1(0), \cdots, V_7(0)$; $a', b', \cdots, h'$; and $a, b, \cdots, h$) with the elements in any row of the matrix. As pairs of rows which give rise to conjugate terms we have 1,7; 2,6; and 3,5. The rows 0,4, it may be pointed out, give rise to real terms. For the purpose of our further calculations it is convenient to rewrite Eq. (4) in another form. If namely we put:

$$[\omega_j^0 V_0(0)+\omega_j^1 V_1(0)+\cdots]=[A_j(0)+iB_j(0)]=R_j(0)[\cos\Delta_j+i\sin\Delta_j]$$

$$[a'\omega_j^0+b'\omega_j^1+\cdots]=[\alpha_j'+i\beta_j']=\sigma_j'[\cos\varphi_j'+i\sin\varphi_j']$$

$$[a\omega_j^0+b\omega_j^1+\cdots]=[\alpha_j+i\beta_j]=\sigma_j[\cos\varphi_j+i\sin\varphi_j]$$

$$\omega_{sj}=\cos\partial_{sj}+i\sin\partial_{sj}$$

and, further, let $\rho_j=\sigma_j'/\sigma_j$ and $\theta_j=\varphi_j'-\varphi_j$, we can rewrite Eq. (4) as:

$$8V_s(n)=\sum_{j=0}^{7}[A_j(0)+iB_j(0)]\rho_j^n[\cos(n\theta_j-\partial_{sj})+i\sin(n\theta_j-\partial_{sj})]$$

II. PARTICULAR SOLUTIONS OF THE VOLTAGE EQUATIONS

For various assumed initial conditions, i. e., sets of values of the quantities $V_s(0)$, the general solution reduces to simple forms. In particular consider the sets of values given by:

$$V_s(0)=E(0)\cos(s-p)k2\pi/8 \tag{5}$$

where s, p, and $-k$, take the values $0, 1, 2, \cdots, 7$. We then have for $A_j(0)$ and $B_j(0)$, respectively:

$$A_j(0)=E(0)\sum_{s=0}^{7}[\cos(s-p)k2\pi/8][\cos sj2\pi/8],$$

$$B_j(0)=E(0)\sum_{s=0}^{s=7}[\cos(s-p)k2\pi/8][\sin sj2\pi/8].$$

Now from the fact that $\sum_{s=0}^{7}\omega_p\omega_s^r=0$, or $8\omega_p$, respectively, according as $\pm r\neq 0, 8, 16$, etc., or as $\pm r=0, 8, 16$, etc., and from trigonometry, it is possible to prove readily the following theorem:

Theorem I. For any given k such that $-k\neq 0$ or 4, we have $A_j(0)=0$ and $B_j(0)=0$, for every value of j except $j=-k$ and $j=8+K$; for $j=-k$ and $j=8+K$, $A_j(0)=4E(0)\cos(-pk)2\pi/8$ and $B_j(0)=4E(0)\sin$

$(-pk)2\pi/8$; while for $k=0$ or -4, $A_j(0)=0$ and $B_j(0)=0$, for every value of j except 0 or $+4$; finally for $kj=0$ or -4, $A_j(0)=8E(0)\cos(-pk)2\pi/8$, $B_j(0)=0$.

III. Physical Interpretation of the Results

For the physical interpretation of the results we need to know the relative magnitudes of the quantities ρ_j and θ_j. These are obtained by substituting in the formulas for ρ_j and θ_j, the values of the quantities a, a', b, b', etc. in terms of the coefficients of capacity and coefficients of induction of the elements of the machine in that configuration at which the carriers just break contact with the brushes. In order to calculate exactly the various values of ρ_j and θ_j we would require the numerical values of these coefficients. It is, of course, impossible to calculate these. To complete the analysis of any machine it would be necessary to actually measure them. However, we can gain some idea of the relative magnitudes of the ρ's and θ's involved, if we make the same assumptions as were made in the case of the four inductor alternator, namely, that the inductors nearly completely surround the carriers and that the inductors are relatively far apart. Under these conditions we can calculate the following set of values for the ρ's and θ's involved.

j	$\tan\theta$	θ	ρ
0	0	0	1
1, 7	$\sqrt{2}-1$	$\pi/8$	$\sqrt{2}/\sqrt{2-\sqrt{2}}$
2, 6	1	$\pi/4$	$\sqrt{2}$
3, 5	$\sqrt{2}+1$	$3\pi/8$	$\sqrt{2}/\sqrt{2+\sqrt{2}}$
4	0	0	0

The values obtained on the basis of these assumptions are really ideal values which in practice we can only approximate. Nevertheless, they correctly indicate the relative magnitudes of the quantities in question, so that for the purpose of our further discussion we shall assume:

$$\rho_0=1,\ \rho_1>\rho_2>1,\ \rho_3<1,\ \rho_4<1;$$
$$\theta_0=0,\ \theta_1\fallingdotseq\pi/8,\ \theta_2\fallingdotseq\pi/4,\ \theta_3\fallingdotseq 3\pi/8,\ \theta_4=0.$$

The phase angles ∂_{sj}, on the other hand, are independent of the capacities involved in the machine, and are readily determined from the matrix (2). In particular, we have

$$\partial_{s0}=0,\ \partial_{s1}=s\pi/4,\ \partial_{s2}=s\pi/2,\ \partial_{s3}=s3\pi/4,\ \partial_{s4}=s\pi.$$

With all these relations before us we can inquire as to the action of the alternator. We see that in general the action of the machine may be described by asserting that three potential waves of different periods travel around the machine, two of which continually increase in amplitude ($\rho > 1$) and one of which continually decreases in amplitude ($\rho < 1$). Furthermore, eventually, one only of these waves will be perceptible, the others becoming either vanishingly small or negligible in comparison. The wave in question is that corresponding to ρ_1 and θ_1, for we have, for n large,

$$V_s(n) = R_1(0)\rho_1{}^n \cos(n\theta_1 + \Delta_1 - s\pi/4) .$$

However, the action of the alternator will depend, theoretically at least, very markedly on the initial conditions. For example, if we choose the original potentials so as to satisfy the set of values given by equation (5); that is, if we adjust the original potentials so that there will be a difference of phase of $k2\pi/8$ between each pair of successive inductors and if, furthermore, we put the maximum potential on the pth inductor, then only that wave corresponding to $j = -k$ will be present.

If we let $-k$ vary from 0 to 4 and apply Theorem I, we obtain a number of interesting special cases, which it should be possible to verify experimentally.

(1) $k = 0$, $V_s(0) = E(0) = \text{const.}$ The original potentials are all the same. For this case, if in addition we note that it can be shown by the method of a previous paper,[4] $\rho_0 \equiv 1$, no matter what the capacities involved in the machine are, as long as it is symmetrical, we have for every n from 0 to ∞ : $V_s(n) = E(0) = \text{const.}$, that is to say, no change takes place, as we might expect also from qualitative considerations.

(2) $-k = 1$, $V_s(0) = E(0)\cos(s-p)(-\pi/4)$. The corresponding solution is, for every n from 0 to ∞ :

$$V_s(n) = E(0)\rho_1{}^n \cos[n\theta_1 - (s-p)\pi/4] .$$

Under these conditions the potential will reverse approximately every revolution, and the machine will build up very rapidly.

(3) $-k = 2$, $V_s(0) = E(0)\cos(s-p)(-\pi/2)$. The solution in this case is given by

$$V_s(n) = E(0)\rho_2{}^n \cos[n\theta_2 - (s-p)\pi/2] .$$

The potential now reverses approximately every half revolution, but the machine does not build up as rapidly as in case (2), since $\rho_2 < \rho_1$.

(4) $-k = 3$, $V_s(n) = E(0)\rho_3{}^n \cos[n\theta_3 - (s-p)3\pi/4]$. The potential reverses approximately every third of a revolution, but the potentials continually decrease, ($\rho_3 < 1$), and eventually become vanishingly small. In practice they would very likely decrease until the ever-present contact e.m.f.'s took hold and re-excited the machine.

(5) $-k=4,\ V_s(n)=E(o)\rho_4^n \cos[-(s-p)\pi]$. Under these conditions also the potentials would theoretically decrease to zero, or in practice until the contact e.m.f.'s took hold.

IV. APPLICATION OF THE METHOD TO OTHER MACHINES

(1) *Multiple Inductor Machines of the type just discussed.* It has already been stated in our opening paragraph that the method of analysis used in the present work for an eight inductor alternator can be applied to a machine of this type with any number of inductors. For the general case of m inductors and m carriers the matrix (2) would be simply a square matrix of the mth order, involving the mth roots of unity. A theorem corresponding to Theorem I could also be set up very easily for the general case. We have merely to note that if ω_j is the mth root of unity which has the amplitude $j2\pi/m$, we have $\sum_{s=0}^{m} \omega_p \omega_s^r = 0$ or $m\omega_p$, respectively, according as $\pm r$ is, or as it is not, zero or a multiple of m. This follows directly from the fact that $\sum \omega_s^r$ is the sum of like powers of the roots of the equation $x^m - 1 = 0$.

(2) *Solution for Other Schemes of Connections.* Furthermore, if in the case of the eight inductor system just discussed each carrier is connected not to the next following inductor but to the second, third, or pth one following, we obtain equations of exactly the same form as Eq. (1) except that the constants a, a', b, b', etc. have different values. This means, that the solution is of exactly the same form as before but that the ρ's and θ's have different values, and this again holds in general; namely, that once the solution for one alternator of m inductors is determined for one scheme of connections, the solutions for all other schemes of connections are obtained by assigning to the ρ's and θ's their proper values. Of course, the scheme of connections must be symmetrical and not haphazard.

(3) *Machines with Double the Number of Carriers.* If the eight inductor machine just discussed were built up with 16 carriers instead of 8, the matrix of the coefficients of the voltage equations (sixteen in number) would take the form

$$\begin{matrix} M_1 & M_2 \\ M_3 & M_4 \end{matrix}$$

where each of the matrices M_i is a cyclic matrix of the 8th order. To solve this case, we divide the set of sixteen equations into two sets of eight (the first set involving M_1, M_2, the second M_3, M_4) and apply the method by which Eq. (3) is obtained to each set separately, but instead of deriving an equation of the form (3), we would now have from the first set one of the form:

$$(\alpha_1+i\beta_1)Z_1(n+1)+(\alpha_2+i\beta_2)Z_2(n+1) = (\alpha_1'+i\beta_1')Z_1(n)+(\alpha_2'+i\beta_2')Z_2(n),$$

and from the second set another of the same type except that the α's and β's have different values. Each of these pairs (and there would be eight such pairs) can be solved by the method of finite differences, as already outlined in previous papers. This method again can be generalized to apply to the alternator with any number of inductors.

(4) and (5) *Machines in which the number of carriers is three or four times the number of inductors.* The method just given for case (3) can be further generalized to apply to the case of 24 and 32 carriers, or in general to the case in which the number of carriers is three or four times the number of inductors. Case (3) above reduces, if the method of finite differences is applied, to the solution of quadratic equations, while the two cases now under consideration reduce to the solution of cubic and biquadratic equations respectively.

(6) *Electrostatic Alternators of the Wimshurst Type.* What has just been said applied also to alternators of the Wimshurst type, since they give rise to equations of exactly the same type as (3), (4), (5).

In general, of course, as the number of inductors and carriers is increased the detailed solution becomes more and more laborious although theoretically it can be carried out. However, it is to be expected that the general features of these machines are not greatly changed by an increase in the number of elements; for example, it is to be expected that doubling the number of carriers will make the voltage wave more continuous without greatly affecting the period of alternation or the transformation ratio.

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A STUDY OF POLARIZATION CAPACITY OVER A WIDE FREQUENCY BAND

By Irving Wolff

Abstract

The polarization capacity of platinum electrodes in sulphuric acid and also of gold electrodes in sulphuric acid has been studied from 200 to 200,000 cycles per second. An alternating current bridge was used to make the measurements in the audible range and a bridge with heterodyne detector for the higher frequencies. If the *relation connecting capacity and frequency* is put in the form $C=C_0/f^P$ where C_0 and P are constants then at the lower frequencies P is nearly equal to .3 while at the higher frequencies it approaches .5. At the same time, the phase angle of the capacity shifts from about 20 to about 40 degrees. Voltage measurements made to determine the *limiting value of the initial capacity* show that it is of the same order of magnitude for alternating current as for direct charge. When *two harmonic alternating currents of differing frequencies are simultaneously impressed on a cell*, the polarization capacity measured by means of either one is independent of the presence of the other.

THE study of polarization capacity phenomena by alternating current methods has taken on a new interest in recent years. The development of alternating current measuring methods during the past decade, particularly the adoption of the vacuum tube for these purposes, has made possible accurate measurements of capacity over a wide range of frequency formerly inaccessible. Predictions which had been made for the action of cells at high frequencies can now be verified or shown in need of modification. On the theoretical side, the views of electrode phenomena which connect polarization with surface reactions afford some very interesting subjects for theoretical investigation.

The first attempt to use frequencies above a few thousand per second for polarization measurements was made by Kruger[1] in 1906. He used a very ingenious method with a damped oscillatory discharge, but not enough points were taken and the frequency range was not sufficiently extended so that very definite conclusions could be drawn. The first serious attempts to get polarization capacity measurements above audible frequencies were made by Merritt[2] and Jolliffe.[3] It is to follow up their work that the present investigation was undertaken.

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[1] Kruger, Ann. d. Physik **21**, 301 (1906).

[2] Merritt, Phys. Rev. **17**, 524 (1921).

[3] Joliffe, Phys. Rev. **22**, 293 (1923).

M. Wien[4] had studied the change of capacity with frequency for platinum electrodes in solutions of sulphuric acid at various audible frequencies, and his results, as well as the theorectical explanations given of them by Warburg[5] and Kruger,[6] had led to the expectation that at the higher frequencies the rate of change of capacity with frequency should be lessened, and in fact it was predicted that the capacity would become constant as the frequency was raised. Symbolically, if the relation between P, the back e.f.m. of polarization, and I, the alternating current through the cell is put in the following form (first suggested by Wien[4]) $P=I/C\omega\sin(\omega t-\pi/2+\psi)$, C should tend to become constant and ψ should approach zero as ω becomes greater. Jolliffe has found however that at frequencies from 100,000 to 2,000,000 per second C becomes proportional to $1/\omega^{\frac{1}{2}}$ and ψ is near 45° in the case of gold and for platinum C has been found proportional to $(1/\omega^{\frac{1}{2}}+\text{small const.})$. It is well known that the value of the polarization capacity depends very much on the particular piece of metal used in the cell and even for the same piece varies very much under different conditions. It seemed entirely possible therefore that these discordant results might have been due to the fact that the cells used were different. In order to test the hypothesis a single cell should be carried through both frequency ranges.

APPARATUS

A bridge shown in Figs. 1 and 2 was used to make these measurements, a vacuum tube oscillator supplying the alternating current. The arms R_1 R_2 R_3 are non-inductive resistances while a variable inductance is used to balance the capacity in arm 4. Since, as will be shown below, it is necessary to use small potentials across the cell to get the most information from polarization capacity measurements, a three stage amplifier was used in the detector arm of the bridge. In order to get most satisfactory operation of a bridge with an amplifier the Wagner[7] earth connection should be used as shown in diagram. In making measurements, arms 1 and 3 were kept equal. The cell was placed in arm 4 and the variable inductance in this arm and the resistance in arm 2 were adjusted so that the bridge was balanced. A switch was arranged so that a variable capacity box in series with a resistance, wound by the Ayrton method, could be substituted for the cell. It was thus possible to read off directly from this capacity and resistance the capacity and resistance of the cell. The frequency was at the same time easily calculated by noting the value of the variable inductance required to balance this capacity; f then being equal to $1/2\pi\sqrt{LC}$. These calculated values were checked at several points by means of tuning forks. At frequencies above the audible range a heterodyne beat method of detection was used, the beating current being supplied by a vacuum tube oscillator. This circuit and the de-

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[4] Wien, Ann. d. Physik **294,** 37 (1896).

[5] Warburg, Ann. d. Physik **303,** 492 (1899); **311,** 125 (1901).

[6] Kruger, Phys. Zeits. **45,** 1 (1904).

[7] Wagner, Elect. Tech. Zeits. **32,** 1001 (1911).

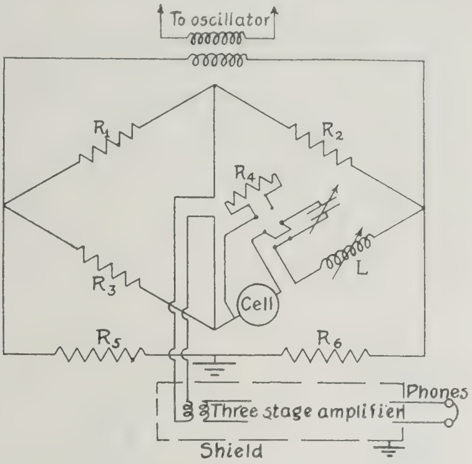

Fig. 1. Audio frequency bridge.

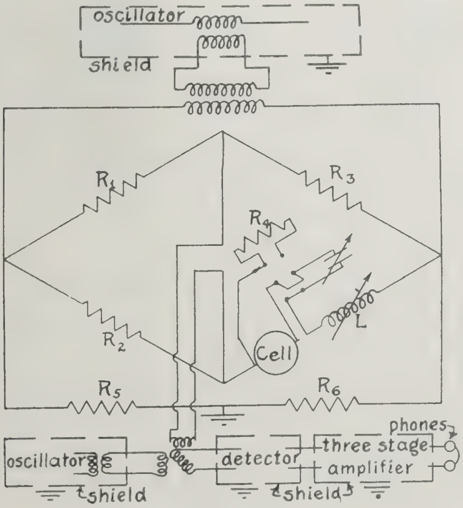

Fig. 2. High frequency bridge.

tector circuit from the bridge were loosely coupled to a third coil which led to a detector and amplifier. The frequency was measured by means of a S. C. R. Signal Corps wavemeter.

In order to make these measurements strictly comparable with Jolliffe's results the cells he had used (shown in Figs. 3 a "Cell A") were again employed in the first part of this work. The electrodes consisted of either gold or platinum rods of 1 mm radius sealed into glass tubes with DeKotinsky cement and then ground down so that only the cross section was exposed. They were usually placed so as to be between .5 and 1 mm apart.

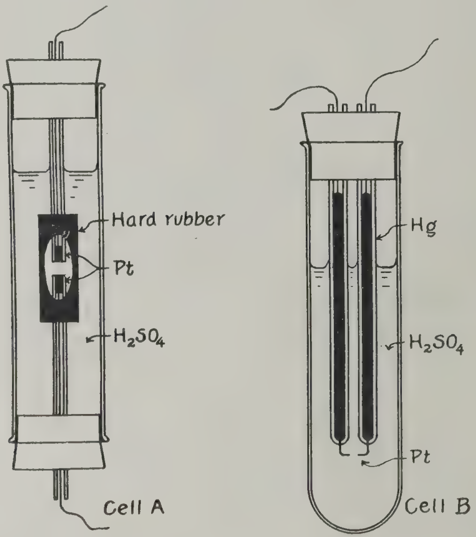

Fig. 3. Diagrams of electrolytic cells.

RESULTS

Before giving the results of the capacity-frequency runs several of the precautions which were needed to secure consistent results will be described. The earliest experimenters found that the polarization capacity was a function of the applied voltage but that a constant value was approached as the polarization potential was reduced. This so-called initial capacity has the most significant theoretical explanation and is therefore of the most interest. Since this change of capacity with potential had only been determined for direct charge, however, it was thought worth while to make a few rough determinations of this relation at several frequencies. To measure the potential drop across the cell a transformer with an input impedance of about 15,000 ohms was shunted across, and a vacuum tube was attached to the output as a detector. The change in plate current was read by means of a d.c. galvanometer. The whole transformer, vacuum tube, galvanometer system was calibrated throughout the frequency range and gave very satisfactory service, showing a change after a year's use which was less than the calibration errors. As all the curves giving the relation between capacity and potential were similar only one is shown in Fig. 4. The capacity *C* and phase angle ψ as defined above are both plotted against the potential drop at the electrodes, i.e., the total drop over the cell minus the drop due to the resistance of the electrolyte. The resistance of the cell was calculated from known conductivity data and from the dimensions of the cell. The most important points to be noted in these curves are the asymptotic values approached by the capacity and phase angle below .1 volt and their more rapid increase above this value. This limit for the initial capacity corresponds well with that found by direct charge methods.

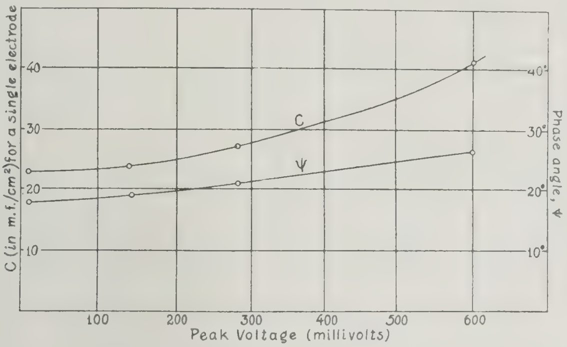

Fig. 4. Curve 1. Polarization capacity as a function of peak voltage at 1340 cycles per sec. Cell *A*, Pt−10% H_2SO_4.

In making the capacity-frequency measurements the potential applied to the cell was always kept below this critical value by determining the potential applied by means of the volt-meter, or, when this instrument could not be used, by reducing the current through the cell until further reduction caused no change in the bridge setting.

When the first measurements were made it was found that if it had taken some little time to make the reading with the comparison capacity, the cell did not immediately return to the same condition that it had previously shown. This was traced to a slight polarization which was set up in the cell when it was in the bridge circuit. Apparently even after the cell had been in the solution for a number of days some dissimilarities still existed in the electrodes which caused a small current to flow and polarize the cell. When the comparison capacity was substituted for the cell the circuit was open and under the influence of diffusion and other causes this polarization gradually disappeared, to build up again when the cell was placed in the bridge circuit. It was thought best to eliminate this small variation by always measuring the capacity when the cell was self polarized. To do this connections were arranged always to keep the cell on short circuit while the comparison capacity was being used.

In making capacity tests it was at first thought that a very pure sine wave should be used in order to get reliable results because of the change of capacity with frequency. Now, although the vacuum tube oscillator gives a wave which is quite satisfactory for most alternating current bridge purposes it cannot be said to be entirely free from overtones. As no data were available on the effects of these overtones on the capacity measurements an investigation of their possible effect was made with some very interesting results. The method of procedure was as follows: Two oscillating circuits of different frequencies were simultaneously loosely coupled to the bridge input. The pitches were kept sufficiently different so that they could readily be distinguished and the bridge could be balanced with respect to either of them while the other was sounding. In this way capacity and resistance measurements were made with an alternating current of a certain frequency while one of any other desired frequency and intensity was at the same time present.

The results of this test showed conclusively that overtones were not affecting the measurements. The balance point determined by means of either pitch was absolutely independent of the presence or absence of the other. This was even true when the supposed disturbing pitch had an intensity greater than that of the pitch being used for measurement.

These facts have further application of interest. It has been suggested by various experimenters, laterly by Haworth[8] and Gunther-Schultze,[9] that the capacity in certain cells might be due to the formation of a thin gas film, or sometimes a poorly conducting layer varying from one to a few molecules in thickness, this film acting as the leaky dielectric of a thin parallel plate condenser. In order to explain on the basis of this theory the change of capacity with frequency, it is necessary to assume that the thickness of this film changes. Since it is the thickness of this film that determines the capacity and only one thickness is possible at any particular time, we must draw the conclusion that when two frequencies are simultaneously impressed on the cell the capacity shall be the same for each. This is in contradiction with the observed facts. The theories of Warburg[5] and Kruger,[6] however, predict just the results that have been found true. The back electromotive force of polarization in their theories is determined by the solution of a partial linear differential equation of the second order in two variables, time and distance from the electrode, with one boundary condition determined by the form of the impressed current and the other by the fact that the function must vanish at ∞. Now it is known that if the function defining the first boundary condition be expressed as a sum of simple harmonic terms, the solution of such an equation will be of the same form, the coefficient of each term being independent of the other. Applying this to the experiment given above, the back electromotive force corresponding to each applied sine current will be independent of the presence of the other and therefore each pitch will keep its own capacity in agreement with the results of these experiments.

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[8] Haworth, Far. Soc. Trans. **16**, 365 (1920).

[9] Gunther-Schultze, Zeits. f. Physik **2**, 36 (1920).

It is well known that the resistance of an electrolyte and also its polarization capacity have considerable temperature coefficients. To guard against the errors due to possible temperature changes while the measurements were in progress, the cells were in the later experiments constantly kept in ice filled Dewar flasks.

Another possible source of error enters when it is desired to make the measurements of capacity shortly after the electrodes have been immersed in the electrolyte. After a cell has been set up, its capacity changes quite rapidly for some time, so that it is necessary to make a correction for this effect. It was found that the rate of change of capacity was almost constant over a short time interval and that the proportionate change was nearly the same for the different frequencies. A true temperature coefficient of capacity could therefore be determined for some mean frequency, and the correction computed for each measurement when necessary.

With these precautions and corrections, very consistent results could be secured as will be shown by the succeeding curves. Curves 2, 3, and 4 (Fig. 5) show the results of some tests taken with Jolliffe's cell using sulphuric acid. A diagram of the electrodes of this cell is shown in Fig. 3 under the heading "Cell A." In these curves, there are plotted against frequency the polarization capacity C in Wien's formula and the phase angle ψ.

In order to make the interpretation of the results easier, logarithmic paper has been used. The slope at any point thus shows the power relation that holds at that point between the capacity and frequency.

The data plotted in curve 2 were taken before the radio frequency bridge had been set up, and while Jolliffe was still taking data. There is a gap, therefore, between 6000 and 120,000 cycles per second, but the change in the slopes of the capacity-frequency curves between these points is very apparent. The slope of the capacity curves plotted on logarithmic paper, although changing at the low frequencies, is very nearly .3; at high frequencies it is close to .5, as also determined by Jolliffe in other cases, who found at these frequencies that the capacity was almost inversely porportional to the square root of the frequency. This curve also shows the increase in the phase angle which might have been expected from a comparison of the previous work in the low and high frequency ranges.

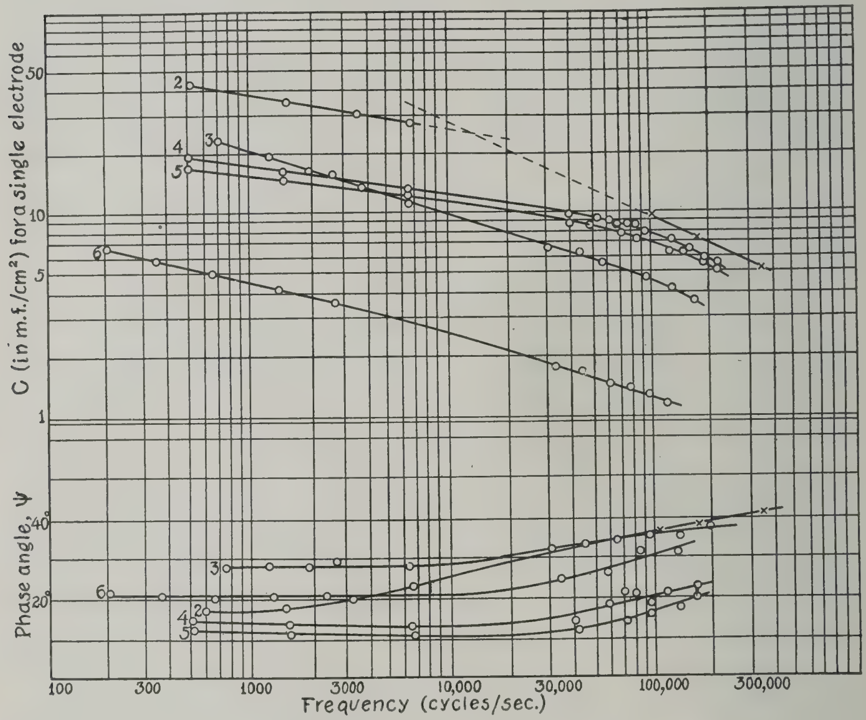

Fig. 5. Curves showing change in capacity with frequency. Curve 2, cell *A*, Pt$-$10% H_2SO_4; curve 3, cell *A*, Pt$-$1% H_2SO_4; curve 4, cell *A*, Pt $-$6% H_2SO_4; curve 5, cell *B*, Pt$-$6% H_2SO_4; curve 6, cell *A*, Au$-$1% H_2SO_4.

Curves 3 and 4 were taken with the same electrodes. The data for curve 3 were taken after the electrodes had been standing in the air for almost a year since last used. Before taking the data shown in curve 4 the electrodes were remounted and polished and then left standing in distilled water until used. Both curves 3 and 4 are very similar to 2.

There was some doubt as to whether the change in the stream lines as the frequency became higher might not have been the cause of the change in the law at the higher frequencies. A cell with an entirely different arrangement of electrodes was therefore built to test this supposition. It is shown in Fig. 3 as "Cell B." The capacity-frequency relation for this cell is shown by curve 5. It will be noticed that it is very nearly of the same form as the others.

Curve 6 shows the same relations for a cell of the Jolliffe type using gold electrodes in sulphuric acid. It will be noted that although the capacity in this case happens to be approximately one quarter as great as in the case of platinum the curve form both for capacity and phase angle is substantially the same.

Conclusions

1. When two harmonic alternating currents of differing frequencies are simultaneously impressed on a cell, the polarization capacity measured by means of either one is independent of the presence of the other.

2. The previous discordant observations giving change of capacity with frequency in a platinum sulphuric cell and gold sulphuric acid cell at low and high frequencies have been coordinated by showing that the law connecting capacity with frequency changes between 3000 and 100,000 cycles per second.

3. This change is due to a true polarization capacity effect and is not caused by change in stream lines in cell at high frequencies.

4. The initial capacity begins to change at the same potential for alternating current as it does for direct charge.

5. Confirming Jolliffe's[3] observations the Warburg and Kruger theories require modification in order to explain the change of phase angle and the increasing rate of change of capacity with frequency as the frequency is raised. These modifications in the theory will be discussed in an article to appear shortly.

In concluding the author wishes to express his appreciation to Professors C. C. Murdock and Ernest Merritt for their kindly help and genuine interest in the above work.

Physical Laboratory,
Cornell University,
Ithaca, New York,
January 27, 1926.

JUNE, 1926 PHYSICAL REVIEW VOLUME 27

THE EMISSIVITY OF BISMUTH IN A MAGNETIC FIELD

By C. W. Heaps

Abstract

Electromagnetic theory and the experiments of Hagen and Rubens lead to the formula $\delta E/E=\delta\sigma/(2\sigma)$, where δE is the change produced in the emissivity E of a metal for long heat waves by a change $\delta\sigma$ in the electrical conductivity σ. Using a thermopile to detect δE a magnetic field of 4900 gauss was used to produce the $\delta\sigma$ in bismuth plates kept at about 100°C. No effect of the field on E was observed for polished surfaces, surfaces etched with nitric acid, or surfaces of a plate cast in vacuum. A change of E ten times smaller than the expected result could have been detected. Possible causes of the negative result are (1) the presence of emitted energy of too short a wave-length, (2) the absence of magneto-resistance in bismuth for high frequency currents, and (3) the absence of magnetoresistance in surface layers of bismuth. Reasons are given for rejecting (1) and (2) and accepting (3) as an explanation of the experiment.

THE behavior of a metal towards radiation of sufficiently long wave-length can be predicted in many respects from a knowledge of the conductivity of the metal. Maxwell's theory gives for the reflecting power, $R=100-200/\sqrt{\sigma T}$, where σ is the conductivity of the metal and T the period of the incident radiation. For waves longer than 4μ Hagen and Rubens[1] have verified this relation experimentally. If A is the absorbing power we have $A=100-R=200/\sqrt{T}$. By Kirchhoff's law we may write $A=E/e$, where E is the amount of radiation emitted per second by the metal and e is the amount emitted by a black body of the same area and temperature. Thus $E/e=200/\sqrt{\sigma T}$.

Any factor, therefore, which changes the electrical conductivity of a metal should change its emissivity for radiation of a particular period. It follows from the above equation that a small change, $\delta\sigma$, in the conductivity will produce a change δE in E, given by the equation $\delta E/E=-\delta\sigma/(2\sigma)$. A similar relation gives the change of absorbing power of the metal when its conductivity changes.

In 1898 Buisson[2] attempted to detect the change of absorbing power of bismuth when its resistance was increased by a magnetic field, but he failed to obtain positive results. His bismuth, in the form of thin electrolytically deposited plates, was transparent enough to allow visual observation of an illuminated window through the metal. A magnetic field capable of increasing the resistance of the plate by 60 percent failed to change the brightness of the observed image by any appreciable amount. Buisson suggested as an explanation of his negative result that a magnetic field does not affect metallic resistance for the high frequencies of light waves. The more recent work of Hagen and Rubens has shown, however, that the equations given above, deduced by Maxwell's theory, do not apply for the high frequencies of visible light, but for waves in the infra-red, beyond 5μ, a very perfect agreement was obtained.[3] For these long waves the emissivity and reflecting powers of metals were found to vary in accordance with the theory when the conductivity was changed by altering the temperature of the metal. Constantan showed very little change of optical properties with temperature because its resistance changed very little.

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[1] Hagen and Rubens, Ann. d. Physik **11**, 873 (1903).

[2] Buisson, Comptes Rendus **126**, 462 (1898).

It would appear probable, therefore, that Buisson's negative results were due to the employment of too short a wave-length. If the resistance change produced in bismuth by a magnetic field is similar in nature to the resistance change produced by a temperature elevation we should certainly expect an effect on the absorption and emission for radiation beyond 4μ.

The writer has performed experiments on bismuth using long waves and the expected effect has not been found.

EXPERIMENTS

For several reasons it is more convenient to measure the energy emission of bismuth than its absorbing or reflecting power. The first experiment was performed on a bismuth plate, cast and polished. This plate, of dimensions $3\times5\times0.2$ cm approximately, was soldered to one side of a copper box and placed between the poles of a Weiss electromagnet. The pole-pieces were 3.5 cm apart and 10 cm in diameter. Water in the copper box was kept boiling by means of an electric heater, and a thermopile connected to a high sensitivity galvanometer was used to receive the radiated heat. The thermopile was mounted in a case provided with the usual shielded aperture and care was taken to exclude all radiation except that from the bismuth plate.

The galvanometer deflection was 27.0 cm and a magnetic field of 4900 gauss failed to produce any observable change in this deflection. The bismuth plate was then etched with nitric acid so that the crystal structure showed up very clearly, but the new surface gave no different result. There appeared, however, to be a thin film of impurity over the surface of the metal so a new plate was made as follows.

Bismuth was melted in a Pyrex bulb to which a second bulb with flat bottom had been sealed. The air was pumped out and the melted bismuth agitated and heated for some time while the pump was running. By tilting the evacuated container the molten bismuth was now allowed to run into the flat-bottomed bulb where it solidified in the form of a plate. This plate was removed by breaking the bulb.

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[3] Wood, Physical Optics, p. 475. Hagen and Rubens found, however, an anomalous behavior in the case of bismuth.

Both surfaces of the plate were apparently very clear and highly reflecting. By viewing these surfaces when illuminated by a single distant lamp, crystal faces could be observed flashing into view as the plate was rotated.[4] The average area of these separate crystal faces was probably about one square millimeter. This plate was clamped to one side of the copper box and the effect of the magnetic field on its emissivity determined. Neither face of the plate showed any change of emissivity capable of being observed.

The galvanometer deflection was 30.0 cm and a change as large as 0.2 cm could not have escaped detection. The value of $\delta E/E$ was thus less than 0.007. The value of $\delta\sigma/\sigma$ for bismuth spirals in the field used is about 0.15, and is probably of about this magnitude for the bismuth plates used. Thus the effect of the magnetic field on the emissivity must be at least ten times smaller than the effect to be expected from the conductivity change.

DISCUSSION

To explain the absence of any effect of a magnetic field on the emissivity we may consider the possible operation of the following three factors.

1. The radiation may contain enough short waves to mask the effect of the field on the long wave emission. From the work of Hagen and Rubens we may assume that the emission of waves shorter than 4μ will be unaffected by the resistance change of the bismuth, while the emission of waves longer than 4μ is represented by the equations given above.

To get an estimate of the relative amounts of energy above and below 4μ we must know the form of the energy distribution curve. Aschkinass[5] has developed a theory for metals radiating waves longer than 4μ and has shown that Wien's displacement law becomes $\lambda_m\theta = 2660$, if θ is absolute temperature and λ_m is wave-length in microns. His theory also gives $S/E = 0.0221\,(r_0\theta/\lambda)^{\frac{1}{2}}$, where E is the ordinate of the energy distribution curve for a black body according to Planck's formula and S is the ordinate at the same temperature and wave-length of the energy distribution curve for the metal. r_0 is the resistivity of the metal at 0°C in ohm cms. It appears, therefore, that the energy distribution curve for the metal is of the same general shape as for a black body, but the maximum is displaced to shorter waves and the whole curve is relatively higher in the short wave region.

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[4] This method of observing crystal structure is due to P. W. Bridgman, Proc. Amer. Acad. **60**, 305 (1925).

[5] Aschkinass, Ann. d. Physik **17**, 960 (1905).

Wien's law, therefore, as modified by Aschkinass, gives $\lambda_m = 7.13\mu$ for the bismuth plate if its temperature is 100°C. Since the temperature must have been lower than this λ_m was somewhat greater than the above value. The theory of Aschkinass will not apply for radiation below 4μ. Rough graphical methods, however, may be applied to the curve for black body radiation, modified beyond 4μ in accordance with the theory of Aschkinass. Such methods make it appear very unlikely that more than one-twelfth of the energy radiated by the bismuth plate had a wave-length less than 4μ. This amount of energy, unaffected by the magnetic field, would not be sufficient to mask the effect of the field on the greater amount of energy in the long waves.

2. The resistance of bismuth for high frequency currents may not be changed by a magnetic field. It is known that the magnetoresistance of bismuth for alternating currents differs from that for direct currents. Heurlinger's theory,[6] however, which ascribes this difference to the interaction of galvano- and thermo-magnetic effects, appears to give a satisfactory explanation of the observed phenomena (which have been confined to lower frequencies than those of light). Heurlinger gives the equation $\rho' - \rho = -PQH^2$, where ρ' is the resistivity of the metal in the field H as the frequency of the current approaches infinity,[7] and ρ is the resistivity in the field for direct currents. P is the coefficient of the Ettingshausen effect and Q the coefficient of the Nernst effect. For bismuth in a field of 6000 gauss Heurlinger finds $-PQH^2/\rho_0 = 0.003$, where ρ_0 is the resistivity when $H = 0$. There is thus a difference of 0.3 percent between the a.c. and d.c. resistance of bismuth in a field of 6000 gauss when very high frequencies are used. The d.c. resistance change produced by this field is about 20 percent, so it appears that if Heurlinger's theory is complete, the high frequency magnetoresistance of bismuth differs very little from the d.c. magnetoresistance.

3. The surface layers of bismuth may be unaffected by the magnetic field while the body of the metal has its resistance changed. For several reasons[8] it appears probable that a magnetic field changes the resistance of bismuth by altering the number of electrons effective at any instant in carrying the current. If equilibrium exists between a group of conducting electrons and a group of bound electrons it is entirely conceivable that a magnetic field may alter the equilibrium

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[6] Heurlinger, Phys. Zeits. **17**, 221 (1916).

[7] Resistance change due to skin effect is not considered in the theory.

conditions so as to change the number of electrons in the respective groups. The molecules on the surface of the metal will be subjected, because of surface tension effects, to conditions different from those in the body of the metal. These molecules may react differently, therefore, towards a magnetic field.

There is considerable evidence in favor of this view. Magnetoresistance for thin bismuth films is smaller than for bismuth in bulk; and the thinner the film the less appears to be the magnetoresistance. Films which have been examined in this respect by Curtiss[9] consisted of small crystals of random orientation. If the crystal composition of the films of different thicknesses (as determined by resistance measurements) was the same the magnetoresistance differences must have been due to the increased relative importance of surface layers for the thinner films. There is some doubt, however, of the identity of crystal structure of the different films.

It seems to be certain that the position relationship of molecules of a metal to each other is of profound influence on the magnetic quality of the metal. Thin amorphous films of nickel are non-magnetic.[10] Liquid metals do not show a true magnetoresistance. Surface layers of iron appear to have a smaller induction than deeper layers, while the converse is true for nickel.[11]

CONCLUSION

While the experimental evidence is not conclusive it nevertheless seems probable that the failure of a magnetic field to affect the emissivity of bismuth is due to the absence of magnetoresistance in the surface layers of the metal. Hagen and Rubens found bismuth occupying an anomalous position as regards reflection and emission coefficients in the list of metals which they investigated. They suggested as reasons for this peculiarity the difficulty of securing good reflecting surfaces of bismuth and the known anomalous behavior of bismuth in other respects. It is possible that the electrical resistance of surface layers of bismuth is different from the body resistance even when no magnetic field acts.

The Rice Institute,
Houston, Texas,
March 20, 1926.

[8] Heaps, Phys. Rev. **19,** 7 (1922); **12,** 340 (1918); Phil. Mag. **50,** 1001 (1925).

[9] Curtiss, Phys. Rev. **18,** 255 (1921).

[10] Ingersoll and DeVinney, Phys. Rev. **26,** 86 (1925).

[11] McKeehan, J.O.S.A. and R.S.I. **11,** 169 (1925), has attributed this effect to strains in the surface layers produced by previous treatment, but on this view it is difficult to explain some of the results of E. H. Williams, Phys. Rev. **33,** 60 (1911).

TEST FOR SPACE QUANTIZATION IN A MAGNETIC FIELD

By B. B. Weatherby and A. Wolf

Abstract

The heterodyne beat method was used to detect a possible change in the dielectric constant of gases, due to space quantization in a magnetic field. A condenser, forming a part of one oscillating circuit of about 1,000,000 cycles frequency, was filled with the gas investigated and the magnetic field then applied. The results obtained show that for helium (20 cm pressure), air (76 cm) and oxygen (76 cm) at room temperature there is no change in the dielectric constant tô 1 part in 500,000. The magnetic field was of the order of 7000–8000 gausses, while the electric field was estimated at 5000–10,000 volts/cm. The tests were carried out with the direction of the electric field both parallel and normal to the direction of the magnetic field.

In a recent article,[1] Ruark and Breit suggested that it might be possible to test for space quantization of gases in a magnetic field through a comparative determination of the dielectric constant of the gas across and along the lines of force of the magnetic field. If we consider an atom to be an electrical doublet subjected to space quantization in a magnetic field, it is reasonable, even in the absence of any accurate calculation, to expect an appreciable change in the dielectric constant of the gas when the field is applied. The magnitude of this change ought moreover to be different, depending on whether the electric field, used for the determination of the dielectric constant, is parallel to the magnetic lines of force or perpendicular to them. Since the changes in dielectric constant so produced may be very small, a highly sensitive test must be used in looking for them.

So little is known with regard to the interaction of electric and magnetic fields in the atom that negative results of experiments along these lines need not necessarily be considered an evidence against space quantization. It is thought that such studies are nevertheless of interest in connection with theories of atomic structure.

The test for a possible change in the dielectric constants of oxygen, air, and helium, in a magnetic field, was carried out by means of apparatus essentially the same as a Whiddington ultramicrometer,[2] consisting of two modified Hartley oscillators. The condenser in one of these was variable and used for the adjustment of the beat frequency. The condenser in the second circuit was made of two aluminum plates 2×10 cm separated by about 0.2 mm and was fixed in value. This second condenser was enclosed in a glass tube filled with the gas investigated and placed between the poles of a Du Bois electromagnet. The usual precautions, with regard to shielding, were observed.

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[1] Ruark and Breit, Phil. Mag. **49,** 504 (1925).

[2] Whiddington, Phil. Mag. **40,** 634 (1920).

Details of the circuit arrangement are shown in Fig. 1. Western Electric 5-watt tubes were used as oscillation generators. The system of chokes and blocking condensers was necessary in order to make possible the use of a single high tension battery.

The oscillation frequency was about 1,000,000 cycles per second and the beats were sufficiently steady over short intervals of time to permit the making of measurements. A residual drift and variation observed in the beats was believed to be due to three causes; (1) charges collecting on the inner walls of the vacuum tubes, (2) motion of the shielding plates due to humidity and temperature changes in the room, (3) imperfect insulation.

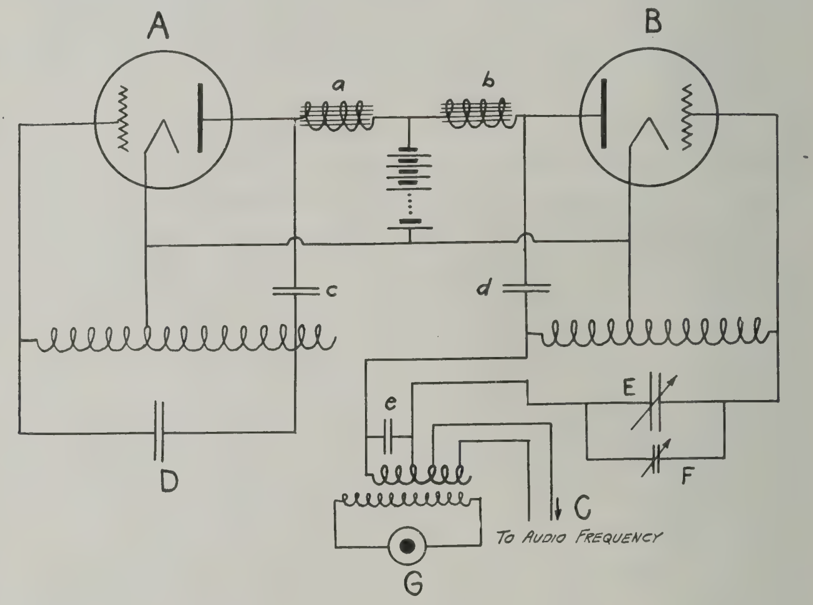

Fig. 1. *A*, *B*, vacuum tubes; *D*, fixed condenser; *E*, *F*, variable condenser and vernier; *G*, loud speaker; *a*, *b*, *c*, *d*, *e*, choke coils and radio frequency by-pass condensers.

The usual procedure was as follows: the variable condenser was adjusted until the beats could be easily counted; the number of beats in a given time was taken with the magnetic field off; the current in the electromagnet was then switched on and the number of beats in the same interval of time counted again. This was done first with the condenser plates set parallel and then with them perpendicular to the magnetic field.

A few typical readings are given below.

	Number of beats in 2 sec.						
	oxygen			helium		air	(brass case condenser)
Magnetic field off:	8	8	6	6	6	12	12
Magnetic field on:	8	7	6	7	8	12	

Each of these sets of observations was taken with a fixed setting of the variable condenser.

When using the condenser described above there was almost always observed a small change in the beat frequency when the current in the magnet was turned on. This change however corresponded to a variation of the frequency of the oscillating circuit of less than one part in a million. The same change was observed when the glass tube containing the fixed condenser was evacuated and it was therefore ascribed to a mechanical effect of the magnetic field on the condenser. A condenser of different design with plates clamped rigidly inside a metal case eliminated the effect completely. This second condenser was, however, used only in the experiments with air.

The observations show that with an electric field estimated at 5,000–10,000 volts per cm the oscillation frequency did not change by more than 1 part in a million when a magnetic field of 7000–8000 gausses was applied. Air and oxygen were investigated at atmospheric pressure and helium at a pressure of 20 cm Hg. All observations were made at room temperature.

As the formula for the frequency of an oscillating circuit is $f = 1/2\pi\sqrt{LC}$ the above results mean that the dielectric constants of the gases investigated do not change by more than 1 part in 500,000 when a magnetic field is applied under the conditions of the experiment. (No correction was here applied for the capacity of the leads.) Different results might have conceivably been obtained at low temperatures or with a smaller electric field.

The dielectric constants of gases at ordinary pressures are so close to unity that a precision of 1:500,000 in the dielectric constant corresponds to much less precision when the average polarization of the atoms and molecules is considered. Under the conditions of the experiment our results show that when the magnetic field is applied, the average electrical polarization of oxygen and air does not change by more than 1:250 of its value, while that of helium, which was used at a lower pressure and has a dielectric constant closer to unity, does not change by 1:10 of its value.

In conclusion we wish to express out thanks to Professor C. B. Bazzoni who suggested carrying out this test.

Research Section, Randal Morgan Physics Laboratory,
University of Pennsylvania,
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THE HALL EFFECT IN BISMUTH WITH LOW MAGNETIC FIELDS

By Palmer H. Craig

Abstract

The Hall effect in bismuth for a magnetic field strength of from 0.07 to 1.00 gauss was accurately determined by improved methods. *Production of the bismuth films.* Various methods for obtaining excessively thin, homogeneous bismuth films were tried and compared, such as casting, electroplating, evaporating, sputtering, and metallic spraying, of which the last three methods were particularly successful. *Measurement of very low voltages.* By refinements made in the potentiometer and measuring circuits, readings to one-tenth microvolt were accurate and reproducible. *Magnitude of the Hall effect at low fields.* The value of the Hall coefficient, R, is abnormally large between 0.07 and 0.30 gauss, having a value of -171 at 0.07 gauss, as compared with a value of -11 which R had for this film at 15 gausses. The value at 4220 gausses was -29. A curve is plotted showing the rapid decrease in the value of $-R$ between 0.07 and 0.30 gauss, and comparison is made with the higher values of field strength. It is noted that by putting the Hall potential of one film in series with one or more other films we obtain comparatively high values of the Hall e.m.f. which may be applied to great advantage as an alternating current rectifier in radio and similar applications.

Introduction

Since the discovery of the Hall effect in 1875 much has been done to elucidate this phenomenon both experimentally and theoretically. But, with the exception of Righi,[1] who employed fields comparable to that of the earth, and a few others, almost all investigators have used strong fields. It is important to know accurately the effect of low fields, to compare it with the known facts and to determine whether any abnormal relations exist. As the effect of the magnetic field is small in all cases, a great refinement in the potentiometer and measuring circuits is imperative with weak fields, and the preparation of the bismuth strips presents great difficulties and requires special methods.

Preparation—Experimental Arrangements

Since the Hall effect increases with the thinness of the metallic strip, the first requisite was to prepare extremely thin films of metal. Bismuth and tellurium, which have the highest Hall coefficient of the ordinary metals, were selected and six different methods were tried in order to find the best and quickest way of making films which would be extremely thin and at the same time electrically continuous. These processes were casting, dipping, spraying, electroplating, evaporating, and sputtering.

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[1] Righi, Jour. d. Physique **3**, 127 (1884).

Thin films of bismuth cannot be produced by casting unless pressure is exerted on the surface of the metal as it cools, and provision must then be made for lateral expansion when solidifying.

Surprisingly thin and uniform films were, however, obtained by dipping mica sheets into molten bismuth and using the metallic film which adhered to the mica. If the surface of the mica be slightly roughened with hydrofluoric acid, and care be used in withdrawing the mica from the molten metal, a very thin and uniform film can be obtained by this very simple and rapid method.

Much work was done by the author to produce very thin plates of bismuth and tellurium by the process of spraying molten metal. Excellent results were obtained both with the "Schoop" compressed air metallic spraying process, and also with the "Gravitas" metal dust spraying process. Cooperation in this part of the work was kindly rendered by the Metals Coating Company of Philadelphia. Both of these spraying processes involve spraying metals in the molten state by means of a compressed air gun. In the case of bismuth it was found advisable to use compressed nitrogen, instead of air, in order to prevent oxidation of the sprayed layer. When applied to mica, glass, and bakelite, excellent films of both bismuth and tellurium were obtained.

Attempts to produce homogeneous films by electroplating met with poor results, even when great care was used as regards temperature, speed of the rotating cathode, and concentration of solution.

Evaporation of molten bismuth in a partial vacuum produced very good results. Bismuth was placed inside an evacuated bell-jar and was melted by an electric heater. A glass plate, suspended above the arrangement, collected the evaporated bismuth in the form of excellent films.

Cathodic sputtering undoubtedly produces the thinnest films of any method. With reasonable care bismuth films can easily be prepared by this method so thin as to be quite transparent. Sputtering was accomplished by applying the secondary current of a 20,000 volt transformer to anode and cathode electrodes placed inside a bell jar evacuated to 30 microns. Rectification of the secondary current by a kenetron accelerated the action. A disc of bismuth 3.5 inches in diameter was used as a cathode, and the glass plate on which the film was to be sputtered was placed just outside the Crookes' dark space, which was about 2 cms long. With a current of 5 milli-amperes excellent films were produced on glass in about 20 minutes.

Disposition of the Apparatus

The very weak magnetic fields employed in this work were obtained from an air core solenoid. When a given current is passed through such a coil the field at the center is easily calculated. This calculated value was checked by a calibrated ballistic galvanometer in conjunction with a flip coil. The actual coil employed consisted of 100 turns of wire wound on a rectangular wooden form 8×11 cm in cross-sectional area, the size of this form being just large enough to accommodate the film used. The inductance of this coil was 2.5 millihenries, and it was therefore necessary to pass 35.2 milli-amperes through it in order to get a field of one gauss at the center. Because of the extremely low values of magnetic field used, it was necessary to shield the arrangement carefully from any action of the earth's and stray fields. Several methods were tried to accomplish this shielding, the one finally adopted being that of placing the set-up so that the plane of the bismuth film coincided exactly with the magnetic inclination of the earth's field at that point, thus eliminating any magnetic component in a direction perpendicular to the plane of the metallic film. Care was taken to keep all iron away from the vicinity of the apparatus, and upon actual measurement stray fields were found to be negligible.

Chemically pure bismuth for producing the films was furnished by Eimer and Amend and the film itself, obtained by any one of the previously described methods, was mounted on bakelite with sodium silicate as a binder. Contact at the ends for the longitudinal current was made by phosphor-bronze spring clips, and contact at the edges of the film, for picking up the transverse Hall potential, was obtained by means of small brass fingers attached to machine screws passed through the bakelite. The surface of the film was carefully cleaned with weak hydrochloric acid solution to remove surface oxides, and the entire film and connections were then painted with sodium silicate to keep semi-conducting layers of dirt and moisture from collecting on the surface of the film. In some cases it was even found advisable to mould the entire arrangement in sulphur to obviate this difficulty.

Since the potential differences to be measured were of the order of one microvolt, extreme care was taken to render the measuring apparatus very accurate and stable. The transverse Hall effect potential was measured by means of a Leeds and Northrup type K potentiometer, redesigned with a system of calibrated external shunts which increased the sensitivity of the instrument ten times. Four galvanometers of varying degrees of sensitivity were used with potentiometer for null readings, the most sensitive galvanometer having a sensitivity of 12.2 mm per M.V. The longitudinal current through the film was supplied by large storage cells, the output of which passed through a large filter system of two very large inductances in series with the line, the lines being shunted by two condensers of six microfarads each. This filter eliminated erratic action caused by sudden fluctuations of the longitudinal current occasioned by bubbling of the cells.

The main current through the potentiometer itself was passed through a similar filter and was allowed to flow over night before taking readings so that greater stability could be expected. The null potentiometer reading on the standard cell was checked before and after each measurement.

Great care was taken to eliminate all spurious effects. Thermal effects, of course, constituted the greater part of these corrections. Junctions of dissimilar metals in the circuit were reduced to a minimum, and the remaining potentials due to Thomson and allied effects were accurately measured the instant the longitudinal current was broken. Grounding one side of the potentiometer circuit was found to increase stability.

For the work at high magnetic fields, a large electromagnet was used. This magnet was capable of producing a field of 18,000 gausses in a narrow air gap, the field of which was measured by a calibrated ballistic galvanometer in conjunction with a flip coil.

Experimental Results and Discussion

Using a bismuth film obtained by metallic spraying, 3.5×8.0 cm in area and 0.012 cm thick, the results shown in Table I were obtained. These results are in agreement with those obtained with films of the other types described previously. In this table three different ranges of magnetic field strength were investigated with the same bismuth film and under the same general conditions. A longitudinal current of 1.5 amperes was used throughout Table I. The "residual" e.m.f. (measured in microvolts) which is referred to in the second column is the potential difference caused by the fact that the brass fingers which pick up the transverse Hall potential cannot possibly be placed at exactly equipotential spots with regard to the longitudinal current. These contacts were placed as near to equipotential points as possible and the remaining difference of potential was measured as given in the second column of the table. The second and third columns automatically include the sum of the thermal effects, since it is of course impossible to eliminate these thermal potentials from the potentials indicated in these columns. However, the spurious effects are eliminated when column two is subtracted from column three in order to get the net Hall e.m.f. in the fourth column. The Hall coefficient, R, given in the fifth column is calculated from the usual formula,[2] $R=Ed/IH$, where R is the Hall coefficient, d the thickness of the film in centimeters, I the longitudinal current in abamperes, H the magnetic field strength in gausses, and E the net Hall e.m.f.

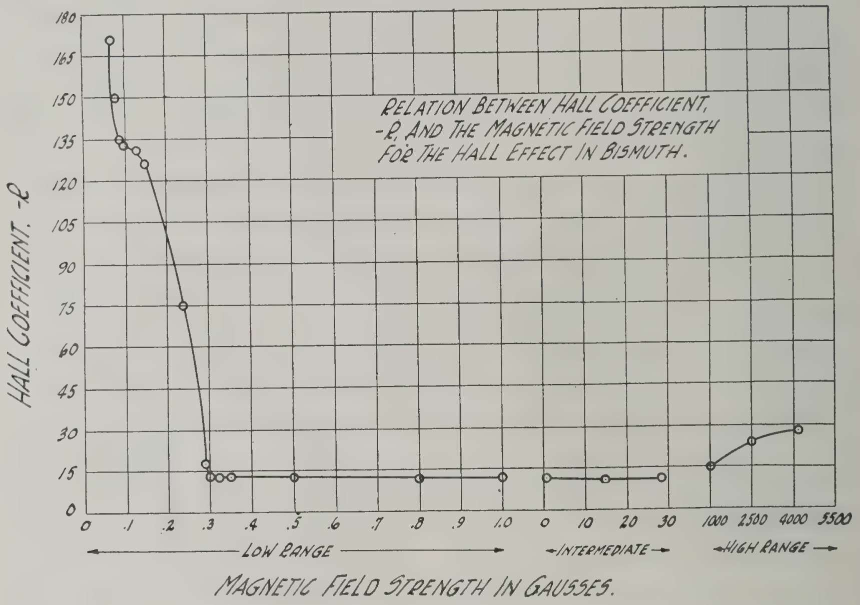

Fig. 1

It is immediately apparent that the Hall coefficient is abnormally high in the range of very low fields, and falls rapidly in value as the field is slightly increased. Reference to the graph shows a slight irregularity near 0.1 gauss, a straightening out of the curve at about 0.3 gauss, and then an approximately linear relation until a field strength of 1.0 gauss is reached. Readings in an intermediate range of zero to 30 gausses showed that $-R$ is practically constant at a value of 11 throughout this range. This value agrees very well with the value of 10.27 which Von Ettingshausen and Nernst[3] found for bismuth at a field of 1650 gausses. In the range from 1000 to 4200 gausses the coefficient increases slightly from 15 to 29. This curve was selected from a dozen similar graphs as being one of the most representative, and the irregularity in the neighborhood of 0.1 gauss is typical of similar irregularities in all curves obtained with the various films.

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[2] L. L. Campbell, "Galvanomagnetic and Thermomagnetic Effects," p. 9.

These results show that the value of $-R$ at very low fields is higher than has been heretofore suspected and that the curve for $-R$, plotted against field strength, shows a marked rise in this low range.

Each of the values in Table I are average values for approximately twelve readings at each value of field strength. These readings are reproducible to approximately one-tenth of a microvolt, and the readings forming the averages did not vary more than this amount.

During the course of the experiments an interesting incidental fact was discovered, namely that the Hall potential of one film may be put in series with that of one or more other films, the sum of these series potentials agreeing very well with the calculated sum of the Hall potentials of the individual films as observed separately. Although this fact has little application where quantitative readings of a high degree of accuracy are desired, it is of real importance in any application where larger values of Hall potential are desirable than those which can be obtained with a single film. The author is at

TABLE I

Hall effect in bismuth for low, intermediate, and high fields

Field strength (gausses)	"Residual" e.m.f. (μ volts)	"Residual" + Hall e.m.f. (μ volts)	Net Hall e.m.f. (μ volts)	-R
.07	14.0	15.5	1.5	171
.08	14.1	15.6	1.5	150
.09	14.2	15.7	1.5	135
.10	14.2	15.8	1.6	133
.13	14.4	16.1	1.7	131
.15	14.3	16.9	2.6	126
.24	14.0	16.3	2.3	75
.29	14.6	21.1	6.5	18
.30	14.5	19.8	5.3	14
.32	14.4	19.6	5.2	13
.35	14.8	20.5	5.7	13
.50	14.6	22.7	8.1	13
.80	14.6	26.6	12.0	12
1.00	14.6	29.6	15.0	12
1.0	14.5	29.5	15.0	12
15.0	14.3	35.1	20.8	11
28.5	14.4	60.4	46.0	11
1000	14.0	1889.0	1875.0	15
2500	14.0	7514.0	7500.0	24
4220	14.0	15324.0	15310.0	29

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[3] Von Ettingshausen and Nernst, Wied. Ann. **29**, 343 (1886).

present using this additive principle in an application of the Hall effect to rectification of alternating current with a method similar to that described by DesCoudres.[4] The additive principle used in this connection produces a Hall potential of several volts in low fields with thin bismuth films, and thus gives the Hall effect a practical importance as a rectifier, especially in radio and similar applications. Work on the additive principle is also being done by Sarek.[5]

The results here presented indicate that there is considerable work to be done in further investigating abnormalities in the Hall coefficient at very low fields, and also suggest that certain modifications or explanations will have to be introduced into the theory of the Hall effect to account for the interesting changes in the Hall coefficient at low fields.

In conclusion, the author wishes to acknowledge his indebtedness to Dr. Louis T. More, Dr. R. C. Gowdy, and Dr. S. J. M. Allen for their kind help and valuable advice tendered throughout the progress of the work.

University of Cincinnati,
Physics Laboratory,
August 2, 1925.

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[4] Des Coudres, Phys. Zeits **2,** 586 (1901).
[5] Sarek, Eleck. u. Maschinenbau, **43,** 172 (1925).

THE RATIO OF HEAT LOSSES BY CONDUCTION AND BY EVAPORATION FROM ANY WATER SURFACE

By I. S. Bowen

Abstract

It is shown that the process of evaporation and diffusion of water vapor from any water surface into the body of air above it is exactly similar to that of the conduction or "diffusion" of specific heat energy from the water surface into the same body of air. Because of this similarity it is possible to represent the ratio R of the heat loss by conduction to that by evaporation by the formula

$$R=.46\left(\frac{T_w-T_a}{P_w-P_a}\right)\frac{P}{760}$$

where T_a and P_a are the original temperature and vapor pressure of the air passing over the lake, and T_w and P_w are the corresponding quantities for the layer of air in contact with the water surface. The substitution of R times the evaporation loss for the value of the conduction heat loss in the Cummings equation for evaporation makes it an exact equation for the determination of evaporation from any water surface in terms of the net radiant energy absorbed by the water and the heat stored in the water.

In his study of evaporation from lakes, Cummings[1] has assumed, as a first approximation, that the determining factor is the incoming solar radiation, i. e. that the evaporation from any lake is roughly equal to the radiant energy falling on the lake divided by the latent heat of vaporization, corrected, of course, for heat stored in the lake due to any change in its temperature. This would be strictly true if we could neglect other heat losses such as conduction and convection, for since evaporation increases rapidly with the temperature, the lake would warm up to such a temperature that the heat lost by evaporation would be just equal to that gained by solar radiation. Wind and humidity would then not affect the total evaporation, but only the temperature that must be reached before equilibrium between evaporation and solar radiation is attained. The present paper is a theoretical attempt to evaluate losses by conduction and convection in terms of easily measurable quantities, and hence to determine whether they are small enough to be neglected; and if not, how they may be corrected.

In order to simplify calculations, we shall assume in the first part of the paper that diffusion coefficients, conductivities, and densities are independent of the temperature. We can write at once for the mass m, of water vapor diffusing per unit time across a space of length l, and area a,

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[1] Cummings, Phys. Rev. **25**, 721 (1925); Journal of Electricity **46**, 491.

$$m = D_1 a(\rho_1 - \rho_2)/l \tag{1}$$

ρ_1 and ρ_2 are the densities of water vapor on the two faces of the space and D_1 is the diffusion coefficient of water vapor through air.

If we multiply both sides of this equation by L, the latent heat of vaporization, we get

$$Lm = D_1 a(L\rho_1 - L\rho_2)/l \tag{2}$$

and if let θ_1 and θ_2 represent the energy per unit volume in the form of latent heat, the energy Q_L carried across becomes

$$Q_L = D_1 a(\theta_1 - \theta_2)/l \tag{3}$$

Likewise we can write the formula for the heat energy Q_S carried, by conduction, across the same space as above:

$$Q_s = Ca(T_1 - T_2)/l \tag{4}$$

where C is the conductivity of the air in the space and T_1 and T_2 are the temperatures of the two faces.

If we substitute $C = D_2 C_p d$, where D_2 is the "diffusion coefficient" or diffusivity for the heat energy, C_p is the specific heat at constant pressure, and d is the density of the air, (4) becomes

$$Q_s = D_2 a(T_1 C_p d - T_2 C_p d)/l \tag{5}$$

Or if we let φ_1 and φ_2 be the densities of specific heat energy at the two faces,

$$Q_s = D_2 a(\varphi_1 - \varphi_2)/l \tag{6}$$

It is seen at once that (3) and (6) are of exactly the same form, the only difference being in the values of D_1 and D_2, which, in fact, differ only by a few percent, (a relationship predicted by the kinetic theory). This leads one to expect that heat losses by evaporation and diffusion, and by conduction, will follow the same laws and will be affected in the same way by convection.

Consider the case of a lake over which a wind is blowing (Fig. 1). Let y be the distance from the windward side of the lake measured parallel to the direction of the wind. Assume that the velocity of the wind at a distance x above the surface of the lake is $f(x)$ and also that this velocity is large enough so that the velocity of horizontal diffusion is negligible in comparison with it. Then for any element of volume $dxdydz$ the amount of latent heat entering the volume per unit time from the lower side is $-D_1(\partial\theta/\partial x)dy\,dz$, while on the upper side the amount leaving is

$$-\left[D_1\frac{\partial\theta}{\partial x}+\frac{\partial}{\partial x}\left(D_1\frac{\partial\theta}{\partial x}\right)dx\right]dydz\ .$$

The difference, if we assume D_1 constant, is then $D_1(\partial^2\theta/\partial x^2)dxdydz$. When a steady state is reached this net gain must be carried away by the air passing through the volume in unit time. The air in passing through the volume $dxdydz$ has its density of latent heat changed from θ to $\theta+(\partial\theta/\partial y)\ dy$; and since the volume passing per unit time is $f(x)dxdz$ the total amount carried away is $(\partial\theta/\partial y)\ f(x)dxdydz$.

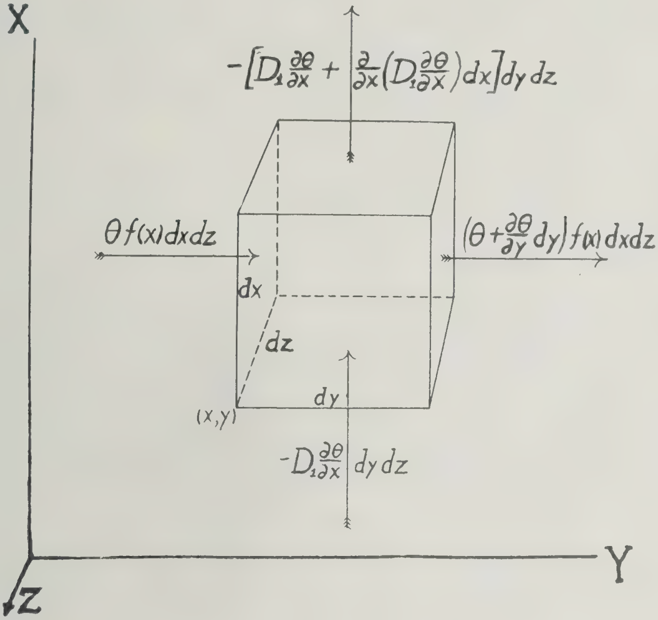
X
$-[D_1\frac{\partial\theta}{\partial x}+\frac{\partial}{\partial x}(D_1\frac{\partial\theta}{\partial x})dx]dy\,dz$
$\theta f(x)dxdz$
$(\theta+\frac{\partial\theta}{\partial y}dy)f(x)dxdz$
dx
dz
dy
(x,y)
$-D_1\frac{\partial\theta}{\partial x}\,dy\,dz$
Y
Z

Fig. 1.

Equating these two quantities we get

$$\frac{\partial\theta}{\partial y}f(x) = D_1\frac{\partial^2\theta}{\partial x^2} \tag{7}$$

and by similar reasoning,

$$\frac{\partial\varphi}{\partial y}f(x) = D_2\frac{\partial^2\varphi}{\partial x^2} \tag{8}$$

as the general equations determining θ and φ at all points above such a lake. The boundary conditions are $\varphi=\varphi_1$, $\theta=\theta_1$ at $x=0$, and $\varphi=\varphi_2$,

$\theta=\theta_2$ at $y=0$. φ_2 and θ_2 represent the energy density, in the form of specific and latent heat respectively, of the incoming air, and φ_1 and θ_1 represent the corresponding densities for the layer of air in contact with the water.

Since it is impossible to obtain a general solution of these equations for any function $f(x)$ we will consider certain special values of $f(x)$.

Case I. $f(x)=K$ from $x=0$ to $x=a$ and $f(x)=0$ from $x=a$ to $x=\infty$. If a and K are small and the lake large, then the layer of air from $x=0$ to $x=a$ will have its temperature changed to that of the water and will become saturated with water vapor, i. e., its specific heat density will change from φ_2 to φ_1 and its latent heat density from θ_2 to θ_1. Evidently the ratio R of heat lost by conduction to that lost by evaporation is

$$R=(\varphi_1-\varphi_2)/(\theta_1-\theta_2) \tag{9}$$

since this is the ratio of the two kinds of energy taken on by each cubic centimeter of the air passing over the lake.

Case II. $f(x)=0$, from $x=0$ to $x=a$; $f(x)=K$, from $x=a$ to $x=\infty$. If the area of the lake is small and the velocity K large, then the water vapor and heat diffusing through the stationary layer from $x=0$ to $x=a$, will be carried away immediately and we can assume $\varphi=\varphi_2$, $\theta=\theta_2$ at the layer $x=a$. Under these conditions the rates at which heat and water vapor leave the water surface are determined solely by diffusion and the ratio between them is simply equation (6) divided by (3).

$$R=D_2(\varphi_1-\varphi_2)/D_1(\theta_1-\theta_2) \tag{10}$$

Case III. $f(x)=Kx^n$ from $x=0$ to $x=\infty$. Professor Epstein has obtained equation (11) as a solution for this value of $f(x)$.

$$\theta=\theta_1+(\theta_2-\theta_1)\frac{\displaystyle\int_0^{x\left[\frac{K}{(n+2)^2D_1y}\right]^{\frac{1}{n+2}}} e^{-\sigma^{n+2}}\,d\sigma}{\displaystyle\int_0^{\infty} e^{-\sigma^{n+2}}\,d\sigma} \tag{11}$$

But the rate of diffusion from unit area of the water surface, i. e., diffusion across the plane $x=0$, is

$$Q_L=-D_1\left(\frac{\partial\theta}{\partial x}\right)_{x=0}=\frac{D_1(\theta_1-\theta_2)\left[\dfrac{K}{(n+2)^2D_1y}\right]^{\frac{1}{n+2}}}{N} \tag{12}$$

where

$$N=\int_0^\infty e^{-\sigma^{n+2}}d\sigma$$

Similarly

$$Q_s=-D_2\left(\frac{\partial\varphi}{\partial x}\right)_{x=0}=\frac{D_2(\varphi_1-\varphi_2)\left(\frac{K}{(n+2)^2D_2y}\right)^{\frac{1}{n+2}}}{N} \tag{13}$$

which gives at once

$$R=\frac{Q_s}{Q_L}=\left(\frac{D_2}{D_1}\right)^{\frac{n+1}{n+2}}\left(\frac{\varphi_1-\varphi_2}{\theta_1-\theta_2}\right) \tag{14}$$

This ratio is independent of y and therefore holds for every square centimeter of the lake and also for the lake as a whole.

DISCUSSION

Case I represents a condition where the whole quantity of air under consideration is completely changed in temperature and moisture content to that of the layer of air in contact with the water. For this reason diffusion is not the limiting factor and hence the diffusion coefficients do not enter into the formula for the ratio of the heats lost by the two processes. It is obvious, however, that if conditions are such that diffusion does enter, it will be in such a way as to increase the loss by the process having the larger diffusion coefficient relative to the loss by the other method. Hence under any conditions of wind we may say, since $D_1>D_2$ that

$$R\leq(\varphi_1-\varphi_2)/(\theta_1-\theta_2) \tag{15}$$

Case II, on the other hand, represents conditions where diffusion is the completely determining factor, the heat and water vapor being immediately carried away after diffusing through the stationary layer. If, however, these are not immediately carried away, they tend to build up the temperature and vapor density on the upper side of this layer, and thus decrease the gradient in the stationary layer. This in turn tends to slow down further diffusion. But the process with the larger diffusion coefficient will build up faster, and hence will be retarded more than the one with the lower diffusion coefficient. Hence we can write

$$R\geq D_2(\varphi_1-\varphi_2)/D_1(\theta_1-\theta_2) \tag{16}$$

The results of Case III support these conclusions since for all values of $n\geq 0$.

$$\left(\frac{D_2}{D_1}\right)^{\frac{1}{2}}\left(\frac{\varphi_1-\varphi_2}{\theta_1-\theta_2}\right)\geq R\geq\frac{D_2}{D_1}\left(\frac{\varphi_1-\varphi_2}{\theta_1-\theta_2}\right)\tag{17}$$

Negative values of n are without physical meaning since they would involve an infinite velocity at $x=0$. The upper limit of R in (17) corresponds to the case $f(x)=K$, *i. e.*, a wind of uniform velocity. The values between this limit and the limit set by Case I correspond to conditions where $f(x)$ is a decreasing function of x, and hence do not correspond to actual conditions over a lake.

The above discussion shows that R lies under all conditions between the values given by Case I and Case II. For these two very simple cases, however, it is no longer necessary to assume D, C, and ρ independent of the temperature.

Thus in Case I, if we consider the changes in an amount of gas that would occupy 1 cc at 0°C, the amount of heat necessary to warm it from the temperature of the air, T_a, to the temperature of the water, T_w, is

$$Q_s=d_0C_p\frac{P}{760}(T_w-T_a)\tag{18}$$

where d_0 is the density of air at 0°C, 76 cm, C_p is the specific heat at constant pressure, and P is the pressure of the air in mm. Likewise the amount of heat taken on in the form of latent heat when this amount of air is brought to saturation at the temperature T_w is

$$Q_L=L\left(\frac{\rho_wT_w-\rho_aT_a}{273}\right)\tag{19}$$

where as before ρ_a and ρ_w are the densities of water vapor in the incoming air and in the layer of air in contact with the water respectively. Therefore

$$R=\frac{Q_s}{Q_L}=\frac{d_0C_p\frac{P}{760}(T_w-T_a)}{L\left(\frac{\rho_wT_w-\rho_aT_a}{273}\right)}\tag{20}$$

Similar consideration, which take into account the known temperature coefficients of heat conduction and diffusion, give for Case II

$$R=\frac{C_0(T/273)^{\gamma_1}(T_w-T_a)}{LD_{1,0}(T/273)^{\gamma_2}(\rho_wT_w-\rho_aT_a)760/P}\tag{21}$$

where C_0 and $D_{1,0}$ are the value of the conductivity and diffusion coefficient at 0°C. Kinetic theory gives $\gamma_1=\gamma_2=\frac{1}{2}$, while experimental data indicate a somewhat larger value, but still make $\gamma_1=\gamma_2$.

If we substitute in these formulas the following experimental data: $d_0=.001293$, $D_0=.206$, $C_0=.0000566$, $C_p=.241$, $L=585.$, $\rho_a T_a/273=P_a/9.41\times10^5$, $\rho_w T_w/273=P_w/9.41\times10^5$, where P_a and P_w are the corresponding partial pressures of water vapor expressed in mm of mercury, we get

Case I.

$$R=.501\left(\frac{T_w-T_a}{P_w-P_a}\right)\frac{P}{760} \tag{22}$$

Case II.

$$R=.442\left(\frac{T_w-T_a}{P_w-P_a}\right)\frac{P}{760} \tag{23}$$

Case III, however, shows that under ordinary conditions where $f(x)$ is an increasing function of x, the true R is nearer Case *II* than Case *I*. Hence we may take as the most probable equation

$$R=.46\left(\frac{T_w-T_a}{P_w-P_a}\right)\frac{P}{760} \qquad (24)^2$$

This equation is, of course, valid only for value of T_w low enough that the volume of the air is not appreciably increased by the water vapor evaporating into it and also that the water vapor on diffusing into the cooler air above does not condense and fall back to the water surface. This last condition is only violated under certain extreme conditions since the air is being warmed by conduction nearly as fast as its dew point is being raised by the diffusion of water vapor into it.

As an example let $T_w=20°C$, $T_a=15°C$, Relative humidity$=.5$, $P=760$ mm. This gives $R=.21$ which indicates that while the ratio is small and can be corrected for by the aid of this formula, yet it cannot be neglected. It may be noted that if we let $R=-1$, this becomes, as it should, the standard formula for the determination of P_a by means of the wet and dry bulb thermometer.

CONCLUSION

If we put in the form of an equation Mr. Cummings'[1] statement of the relation between evaporation and radiant energy, we have

$$I=S+LE+K \tag{25}$$

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[2] Since the above was written, a somewhat similar formula has been derived empirically from wet and dry bulb data. D. K. Dean, Power **62**, p. 754 (1925).

where I is "the radiant energy . . . integrated over any time interval" or perhaps a little more explicitly, the solar and sky radiation corrected for reflection, minus the back radiation, S is the "heat represented by the change in temperature of the water," LE is "the heat represented by the evaporation (E) during the same time interval," L, of course, being the latent heat of evaporation, and K is a "relatively small correction" to cover other losses. These other losses, however, are due to conduction and convection which we have put equal to R times the losses by evaporation, i. e., $R(LE)$, where R can be determined by Eq. (24). Substituting this value of K in (25) we have

$$I=S+LE(1+R) \tag{26}$$

which is an exact equation for any body of water that is thermally insulated on the sides and bottom (a condition holding for most lakes) since it takes into account all processes by which heat can be lost or gained.

Consequently if we know S, E and R, which can be determined easily in any small insulated test jar, we can, following the method proposed by Cummings[1] use this slightly modified formula (26) to determine I or, vice versa, if we know I and can measure S and R, we have a means for calculating the evaporation E from a large body of water where it cannot be measured directly.

Such a body of water, however, is very nearly a black body over a very wide range of wave-lengths, since throughout the infrared even a thin layer of water absorbs almost completely, while in the visible this is true if the water is deep enough, as in a lake or if the inside of the vessel is properly blackened, as can be easily done for any test jar. In addition the reflection at the surface due to the difference in index of refraction is small throughout the visible and infrared to 20μ,[3] which is well beyond the maximum of the back radiation. On account of this fact I as determined by Eq. (26) becomes at once, with only a very small correction for reflection, the value of the net radiation exchanged with a black body at the temperature of the water. Thus such a jar of water can be used to determine the net heat radiated by a black body at night or received by it during the day time.

In a succeeding article Mr. Cummings will present the results of experiments designed to check the modified form of his equation, Eq. (26), under a series of widely different condition. Since this Eq. (26) depends on the determination of R as given by Eq. (24), these experiments will also serve as a test of Eq. (24) as well. His preliminary experiments indicate that these equations will be verified completely.

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[3] Rubens and Ladenburg. Verh. d. Phys. Ges. **11,** 16 (1909).

In conclusion the writer wishes to thank Professor Epstein for his derivation of Eq. (11).

Norman Bridge Laboratory of Physics,
California Institute of Technology,
Pasadena, California,
March 12, 1926.

HEAT TRANSFER IN THE ANNULAR SPACE BETWEEN TWO COAXIAL CYLINDERS*

By S. R. Parsons

Abstract

Two brass tubes are mounted with a common axis, one inside of the other, and are warmed by driving hot air, in turbulent flow, through the annular space between them. The rates of transfer of heat to the two tubes are compared by means of a coefficient representing heat transmitted per unit time per unit area of metal surface per unit difference of temperature between metal and air. Lees has shown that in streamline flow there would be a difference in the surface friction per unit area for the two tubes, and if that were true in turbulent flow, there would be a corresponding difference in the coefficients of heat transfer. The experimental results show that if there is such a difference in turbulent flow, it is not of the magnitude to be expected from Lees' equations, and fail to show with certainty that any difference exists.

When air is passed through the annular space between two coaxial cylinders, such as that formed by one metal tube inside of another, the stream acts simultaneously on two surfaces, of which one is convex, and the other concave. Lees[1] has shown that when a fluid passes in streamline flow through such an annular space, the surface friction per unit area is less on the outer tube than on the inner one, and he raises the question whether there is a similar difference in turbulent flow. If there is, there should be a corresponding difference in the rates of transfer of heat between the stream and the two surfaces, which might be interpreted as representing a difference in the character of the flow close to the walls,—that is, a difference in the extent to which the stream may be regarded as scouring the surfaces. The purpose of the work described in this paper was to show whether or not heat is transmitted more readily to one of the two surfaces than the other.

Apparatus and Experimental Procedure

Two pairs of brass tubes were used, the first 91.3 cm in length, and the second, 170.0 cm. The inner and outer diameters of the annular spaces were 0.949 and 1.706, and 0.950 and 2.307 cm, respectively. Each tube was about 1 mm in thickness. Air from a compressor connected to a large tank was forced through a brass tube 1.7 cm in diameter, in which its speed was estimated by means of a Pitot tube; then through a

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* Research Paper No. 36, Journal Series, University of Arkansas.

[1] C. H. Lees, Proc. Roy. Soc. 92, p. 144 (1915).

brass tube surrounded by a heating coil; and then into the annular space between the experimental tubes, which were mounted in a vertical position in order to avoid the sag that would be inevitable if they were horizontal. The outer tube was set into a block of wood, through which a hole was bored to admit the air. A circular wooden plug was fitted into the end of the inner tube, the lower end of the plug being smoothed off into a streamline form, to direct the air as gently as possible into the annular passage. This plug supported the weight of the inner tube, and was itself centered and held in place by fine piano wires passing out through small holes in the wooden block, and wound on screws for adjustment. A thermocouple junction was set in the center of the air stream a few centimeters below the plug. A similar arrangement for centering the plug was used at the upper (outlet) end, and a second thermal junction was placed in the center of the stream about 5 cm above the top of the plug. The air passage ended in a bell mouth. A wooden box about 12 cm square was placed around the tubes, to minimize the effects of air currents in the room. Thermometers were inserted through one side of the box, and while no attempt was made to render it air tight, it was found that the rate of cooling of the outer tube to the air was not appreciably affected by currents in the room, and could therefore be computed with satisfactory accuracy for any condition obtained in the experiments.

Thermal junctions were soldered to the outside of the outer tube, and corresponding junctions attached opposite them on the inner tube, at points whose locations appear in the table below. Holes were drilled in the inner tube, and the junctions soldered into these holes flush with the surface, which was then filed down to as near its original condition as possible, the wires being brought away in a cable inside of the tube to its upper (downstream) end, from which they were led to the measuring instruments. The electrical connections were such that each couple could be connected to a potentiometer, or directly to a galvanometer.

The rates of transfer of heat from the stream of air to the two tubes were compared by means of the rates at which their temperatures rose, and in order to obtain simultaneous rates, two galvanometers were used, one for each tube. The galvanometer readings were calibrated against the potentiometer after each run. A metronome was set to beat seconds, and to ring a bell every third second, and readings of the two galvanometers were taken alternately on the stroke of the bell. From these readings, the temperatures of the two tubes were computed, and plotted against time.

METHOD OF COMPUTATION

Considering any point along the tubes, and using for temperatures the mean values in a plane perpendicular to the axis of the tubes and including the point considered, we may write the equation for either tube alone

$$ms\frac{d\theta}{dt}=q(2\pi r)(T-\theta)$$

where θ is the temperature of the tube; T, the temperature of the air stream; m, the mass per unit length of the tube; s, the specific heat of the tube; r, the radius of the tube; t, the time; and q, the surface coefficient of heat transfer, in units of heat per unit time per unit area per unit difference of temperature between air and tube. The experiments yield values for all of these quantities except q and T. It is not feasible to measure the air temperature T inside of the annular space because, aside from the difficulties of measuring the temperature of a stream of gas at a point where its temperature is changing, anything even so small as thermocouple wires placed in the stream might affect the character of the flow enough to destroy their value. These temperatures may be eliminated, however, and a comparison of the coefficients q for the inner and outer tubes may be obtained as follows. The equation above is applied to each tube, and the values of θ and $d\theta/dt$ are obtained at two different instants during each experimental run. Then, if we let θ be the temperature of outer tube, ϕ the temperature of inner tube, subscripts o and i represent outer and inner tubes, and subscripts 1 and 2 represent the first and second sets of values, respectively, we may write four equations:

$$m_0s_0(d\theta/dt)_1=q_0(2\pi r_0)(T_1-\theta_1)$$
$$m_0s_0(d\theta/dt)_2=q_0(2\pi r_0)(T_2-\theta_2)$$
$$m_is_i(d\phi/dt)_1=q_i(2\pi r_i)(T_1-\phi_1)$$
$$m_is_i(d\phi/dt)_2=q_i(2\pi r_i)(T_2-\phi_2)$$

Solving these equations for the ratio between the coefficients q, and for simplicity letting $(d\theta/dt)_1=a_1$, $(d\theta/dt)_2=a_2$, $(d\phi/dt)_1=b_1$, and $(d\phi/dt)_2=b_2$, we obtain

$$\frac{q_0}{q_i}=\left(\frac{m_0s_0r_i}{m_is_ir_0}\right)\frac{b_1(\phi_2-\theta_2)-b_2(\phi_1-\theta_1)}{a_1(\phi_2-\theta_2)-a_2(\phi_1-\theta_1)}\,.$$

Since the outer tube is losing heat to the surrounding air while its temperature is rising, the value of $d\theta/dt$ used in the equations will be greater than that obtained from the graphs by an amount given by the equation $d\theta/dt = -kT'$, in which T' is the difference in temperature between the tube and the surrounding air, and k is a constant determined from the rate of cooling of the tube when the air is not flowing through it. While the four equations given above suffice for a solution of the temperatures T_1 and T_2 of the air as it passes any thermal junction, the form of the algebraic solution is such as to magnify the effects of expermental errors, and the results are of little value.

The speed of the air stream was estimated from the readings of the Pitot tube, from the ratio of the cross sectional areas of the air passages at the Pitot tube and in the annular space, and from the estimated densities of the air at these two points. These speeds, and the temperature of the air at the entrance to the annular space, which was taken from the thermal junction located at the entrance, do not enter into the computations, but are tabulated with the results to show the range of conditions used in the experiments. The critical speeds for the two pairs of tubes were computed from Lonsdale's equation,[2] for a temperature of 100°C, and it will be seen that the speeds used were high enough to insure turbulent flow.

RESULTS

The results are summarized in Table I. Preliminary trials failed to show any appreciable effect of slight changes in the centering of the inner tube, and if there is such an effect, it is probably balanced out in the mean of the results, on account of the locations of the various thermal junctions, which are as shown in the table, the azimuth representing angular distance around the axis of the tubes, measured from an arbitrary plane. If in smoothing off the inner tube after attaching the thermal junctions to it, the tube was not left in its original condition, any irregularities due to this cause will also tend to balance each other.

Whether there is any significance in the fact that the ratio of the coefficients appears to be less at points near the outlet of the tubes than near the entrance, the writer can not say. The nearest points used are respectively 52 and 66 times as far from the entrance as the thickness of the annular space, for the two pairs of tubes.

For these pairs of tubes, the equations of Lees for streamline flow give values of 0.70 and 0.74, respectively, for the ratio of the surface friction per unit area on the outer tube to that on the inner tube; and since the rate of transfer of heat is proportional[3] to the surface friction, the same values would represent the ratios of the coefficients q. The table shows that over something of a range of speeds and temperatures the mean ratio of the coefficients q is slightly greater than unity, indicating that if there is a difference in the heat transfer coefficients for turbulent flow, it is not comparable with that for streamline flow. But while this mean ratio is a little greater than unity, it must be admitted that the experimental errors are large, and that the results do not show with certainty that the coefficients for the two surfaces are not identical. In other words, the experiments fail to show any difference in the character of the turbulent flow close to the two surfaces.

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[2] T. Lonsdale, Phil. Mag. **46,** p. 163 (1923).

[3] Great Britain Committee for Aeronautics, Technical Reports 1912–1913, p. 45.

TABLE I

Values of the ratio, q_0/q_i, of the rates of transfer of heat to the outer and inner tubes.

Location of thermal junction distance from entrance	Location of thermal junction azimuth	Speed of air stream	Air temperature at entrance	$\frac{q_o}{q_i}$
First pair of tubes: length 91.3 cm; thickness of annular space, 0.38 cm; critical velocity, 7.9 m/sec.				
20 cm	0°	14.4 m/sec.	148°	1.23
20	0	14.4	148	1.18
35	90	21.7	122	1.21
35	270	12.6	150	1.15
55	0	11.9	142	.90
55	180	17.7	113	.99
75	270	24.0	136	1.01
				Mean 1.08 ± .10
Second pair of tubes: length 170.0 cm; thickness of annular space, 0.68 cm; critical velocity, 4.9 m/sec.				
45	90	6.7	132	1.01
60	270	7.3	122	.97
60	270	7.3	118	1.12
60	270	11.9	121	1.21
60	270	11.9	119	1.13
60	270	6.0	119	1.12
135	0	6.3	118	.98
135	0	9.7	133	.97
135	0	6.9	159	.91
135	0	6.9	158	.92
				Mean 1.03 ± .09

THE UNIVERSITY OF ARKANSAS,
February 12, 1926.

BOOK REVIEWS

Relation between temperature, pressure, and densities of gases (S. F. Pickering), Circular of Bureau of Standards, No. 279.—This is a compilation of the known pvT relations of the familiar gases with a discussion of the equations of state of van der Waals, Dieterici, and Berthelot. The numerical use of the tables and curves, as well as of the equations, is explained in detail in the simplest possible terms. Many tables are given so that the Circular contains sufficient information for the solving of problems in this field. A very extensive bibliography is included. The circular should be extremely useful to users, commercial and scientific, of these gases, as well as to teachers. 190 pp., Government Printing Office, Washington, D. C. 1926. Price 25 cents.

J. R. Roebuck.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE WASHINGTON MEETING
APRIL 23 AND 24, 1926

The 139th regular meeting of the American Physical Society was held at the Bureau of Standards, Washington, D. C. on April 23 and 24, 1926. The presiding officers were Professor Dayton C. Miller, President of the Society, and Professor K. T. Compton, Vice-President. The attendance was about three hundred.

On Friday evening there was a dinner at the Raleigh Hotel, attended by two hundred and thirteen members and guests. The speakers at this dinner were Professor M. I. Pupin, Dr. S. W. Stratton, Dr. G. K. Burgess, and General G. O. Squier.

Meeting of the Council.—At the meeting of the Council held on April 23, 1926, seventeen were elected to membership: Martin J. Connoly, Kenneth Cole, Austin M. Cravath, C. del Rosario, Karl G. Emeleus, Hugh Farrell, Sylvan Harris, L. G. Hector, D. W. Morehouse, Leonard J. Neuman, Nicolas P. Rashevsky, P. N. Rhodes, Clarence Rockwell, John L. Rose, Shou Chin Wang, George P. Welch and Harvey A. Zinszer.

The regular program of the American Physical Society consisted of ninety-four papers, Numbers 2, 7, 9, 61, 73, 86, 87, 89, 90, 91, 92, and 95 being read by title. The abstracts of these papers are given in the following pages. An **Author Index** will be found at the end.

HAROLD W. WEBB,
Secretary.

ABSTRACTS

1. **A precision study of the K absorption limit.** F. K. RICHTMYER and J. B. BISHOP, Cornell University.—A series of careful measurements of *observed* absorption coefficients taken through the K absorption limit of silver yields data which, after correcting for the finite width of the slits, are in agreement with the assumption that the λ^3 law holds up to the limit from both directions and at the same time furnishes a method for determining, with comparatively high precision, the magnitude of the absorption discontinuity.

2. **The effect of chemical combination on the absorption of x-rays.** W. B. MOREHOUSE, Cornell University.—The x-ray absorption by aqueous solutions was measured

before and after chemical reaction, employing a differential null method similar to that described by Becker (Phys. Rev., **20**, 134, 1922), and using the direct beam from a water cooled Molybdenum Coolidge tube, operating at 30 kv peak. Cells having equal compartments were used, so that the same elements were in the beam before and after combination. Measurements were made on the following reactions:

(A). $3KI+I_2+2Na_2S_2O_3 \rightarrow 3KI+2NaI+Na_2S_4O_6$.

(B). $K_2Cr_2O_7+12KI+14HCl \rightarrow 8KCl+2CrCl_3+7H_2O+3I_2+6KI$.

(C). $NaOH+HCl \rightarrow NaCl+H_2O$.

Corrections having been made for changes in density the results indicate: Reaction (A). The mass absorption coefficient of the solution after reaction is approximately 0.25 percent less than before reaction. Reaction (B). 0.25 percent greater. Reaction (C). No appreciable change. Since iodine, sulphur and chromium are the only elements changing valence and since computations from known absorption coefficients show that the absorption by the iodine in the beam is several times that by either the sulphur or the chromium, it seems probable that the absorption by iodine in the free state is greater than its absorption in the combined state.

3. X-ray absorption in heated silver. H. S. READ, National Research Council Fellow at Stanford University.—Previous research (Phys. Rev., April, 1926) has suggested that Al, Fe, Ni, Cu, Ag, and Pb have slightly larger absorption coefficients at higher temperatures. Total radiation from a tungsten target tube was used. Continued work with Ag indicates that the transmission is a complicated function of the wave-length (0.2 to 0.7A used) increasing with temperature at some wave-lengths and decreasing with temperature at others. The largest change was a 1.5% decrease in transmission at the K-limit when the Ag strip was heated to 830°C. If this were due to a shift of the K-limit the shift corresponds to +0.00021A which corresponds in turn to −11. volts. This result suggests that energy of thermal agitation may add to x-radiation energy or that heat prepares the atoms in some way to absorb slightly smaller quanta, at the K-limit, than is possible when cool. An equal shift of the whole absorption coefficient curve does not appear to account for the changes of transmission at some of the other wave-lengths. A correction was made for the effect of thermal expansion. A detailed account of the method and results will be published.

4. Conditions for the disappearance of the unmodified line in the Compton effect. G. E. M. JAUNCEY and R. A. BOYD, Washington University. The method previously described by Jauncey and DeFoe (Phys. Rev., **27**, 102, (1926)) for measuring the ratio of the modified to total scattering coefficients when a wave-length of 0.41 A is scattered by carbon at various angles has been used. The ratio becomes practically unity at 87° and continues unity for angles out to 120° (we did not test it further out). However, at angles less than 87° there is a rapid decrease of the ratio as the angle decreases. It seems therefore that unmodified scattering disappears at 87° when $\lambda=0.41$ A. On Jauncey's theory, unmodified scattering disappears at 82°. There is thus good agreement with theory.

5. Measurement of x-ray scattering coefficient. PIERRE MERTZ, Cornell University.—The mass scattering coefficient was measured directly by collecting the scattered radiation in an ionization chamber surrounding the scatterer, comparing its intensity with that of a portion of the primary beam going through an auxiliary ionization chamber of equal length along the ray path. The primary beam consisted of the continuous radiation from a Coolidge tungsten tube, filtered through Al and Cu until the spectral width between the half-maximum intensity points was about 25% of the mean wave-length. Corrections were made for internal absorption in the scatterer and for the increased absorption of the scattered beam in the ionization chamber due to the Compton effect. The latter could not be estimated very accurately and is probably one of the largest sources of error in the determination. The values of mass scattering coefficient (σ/ρ, in cm^2/gram) as determined are given below:

λ	.32	.43	.54	.66	.79 A.
Scatterer			σ/ρ		
C	.166	.182	.194	.214	.234
H_2O	.198	.206	.210	.216	.228
Na	.173	.191	.248		
Li	.133	.165	.157	.169	.200
B	.154	.162	.169	.165	.179

6. **Intensity of x-ray reflection from solid and powdered sodium chloride.** J. A. Bearden, University of Chicago. (Introduced by Arthur H. Compton.)—The experiment of the intensity of x-ray reflection by Bragg, James and Bosanquet has been repeated using monochromatic x-rays ($K\alpha$ line of Molybdenum reflected from rock-salt crystal) for all orders of reflection thereby reducing the uncertainty in choosing a base line. The values of the structure factor F are in satisfactory agreement with the values obtained by the previous experimenters. The most uncertain elements entering in these experiments are: (1) the linear absorption coefficient and (2) the extinction effects. Measurements of the intensity of reflection from powdered crystals have also been made with monochromatic x-rays, using both the transmission and the reflection methods. Both powder methods gave the same values for the structure factor F for several samples of sodium chloride of different history. Except for the (100) plane, however, the values were consistently higher than the corresponding values obtained by the solid crystal method.

7. **Refraction of x-rays by method of total reflection.** Richard L. Doan, University of Chicago.—The critical angle of total reflection of x-rays from polished surfaces is related to the index of refraction by the expression $\theta_c=(2(1-\mu)\ )^{\frac{1}{2}}$, θ being the glancing angle of incidence. Since this critical angle has been found experimentally to be sharply defined, this method furnishes a simple means of determining indices of refraction with a relatively high degree of accuracy. The line Mo$K\alpha_1$, isolated by means of a calcite crystal and suitably placed slits, was allowed to fall on optical surfaces of speculum metal and glass, the reflected beam being received on a photographic plate one meter distant. Approximately one hundred one-minute exposures were made as the mirror was turned at intervals of a few seconds of arc through a total range of about 7′. Measurements, accurate to 1%, gave for speculum, $\theta_c=10'52''$, $1-\mu=4.96(10)^{-6}$; for glass, $\theta_c=6'18''$, $1-\mu=1.67(10)^{-6}$. Attempts were made to use sputtered gold films for reflecting surfaces but the reflection was surprisingly weak and the critical angle not sharply defined. An accurate measurement of the index of refraction of Mo$K\alpha_1$ in gold would be valuable as a check on the Drude-Lorentz dispersion formula because of the expected large resonance effect due to the L-electrons.

8. **Refraction of x-rays in prisms.** Bergen Davis and C. M. Slack, Columbia University.—*A continuation of measurements of refraction of x-rays by means of a double x-ray spectrometer* (Phys. Rev. **27**, 18, (1926)). The double x-ray spectrometer is well suited to this purpose, since the position of the peak of the rocking curve is not affected by unsymmetrical absorption in the prism. Measurements of δ, ($\mu=1-\delta$) were made in substances tabulated below with the observed value in brackets. Using Mo $K\alpha$ ($\lambda=.7078$) the values of $\delta\times10^6$ are: Ag (5.85), Cu (5.95), S (1.39), Al (1.68), Carbon (graphite) (1.23), celluloid (.98) and paraffin (.7). Using Cu$K\alpha$ (1.537), the values of $\delta\times10^6$ are: Al (8.4), celluloid (4.78) and paraffin (3.28). These results agree well with the values calculated. *Broadening of rocking curves.*—The rocking curves were much broadened when the rays passed through granular substances such as graphite, grated paraffin, etc.

This effect, which appears to be due to refraction by the successive particles, has been treated theoretically by Dr. R. van Nardroff. A formula has been obtained which permits the calculation of the size of the particles from the observed broadening.

9. The refraction of x-rays applied to the determination of the diameters of small particles. Robert von Nardroff, Columbia University.—The divergence introduced into a beam of x-rays on passing it through a mass of refracting particles is investigated mathematically. It is found that a plane beam would be scattered by a single sphere of index of refraction $\mu=1-\delta$ so that the fraction of the energy in a cone at an angle between ω and $\omega+d\omega$ with the original direction is $8\delta^2\omega d\omega/(4\delta^2+\omega^2)^2$. For a large number of spheres, if n is the average number of spheres passed through by a ray, the root mean square bend produced is $\alpha_0=2\delta[n(\log 2/\delta+1)]^{\frac{1}{2}}$ and the fraction of the energy lying in a cone between α and $\alpha+d\alpha$ is $2\alpha(\exp.\ (-\alpha^2/\alpha_0^2)\ )/\alpha_0^2$. For a beam originally having a width at half maximum W_0 as measured on the rocking curve of the second crystal of a double x-ray spectrometer, the width after passing through the refracting material will be $W=(W_0^2+2\alpha_0^2)^{\frac{1}{2}}$. This gives a means of determining the number, and, if the total mass is known, the size of particles which could not be measured by other methods. The method is applied to rocking curves obtained by Davis and Slack for beams passed through different thicknesses of graphite. The variations of curve width with thickness of graphite are found to be in agreement with the theory, and, assuming the particles acted like spheres, their approximate diameter is found to be .0035 cm.

10. The theory of x-ray dispersion. R. de L. Kronig, Columbia University.—The quantum theory of dispersion as developed by Ladenburg and Kramers is extended so as to apply to the refraction of x-rays, where the number of atoms in a wave-length cube is no longer large, and the absorption forms a continuous band. A general formula for the index of refraction in terms of the atomic absorption coefficient α and the critical frequencies is given. From the condition, experimentally verified, that the electrons in the atom for impressed frequencies, large compared to their natural frequencies, shall act like free electrons as far as the index of refraction is concerned, a relation is obtained for α. The theory is in accord with Heisenberg's quantum mechanics. Some considerations on the origin of the Compton shifted radiation are added, from which it appears that in the wave description this radiation must be regarded as coming from all the atoms and as being coherent with the incident waves; a result suited to stress the difficulty of harmonizing the wave picture with that of quantum processes in the atoms.

11. The polarization of characteristic x-rays. J. B. Bishop, Cornell University.—An investigation to determine a possible state of polarization of the alpha lines of molybdenum was undertaken in the following manner: A molybdenum target water-cooled Coolidge tube was so mounted that it could be rotated about an axis perpendicular to the cathode stream and passing through the focal spot. A carbon block was placed in the path of the x-ray beam and the intensity of the radiation from it was measured parallel to and perpendicular to the cathode stream respectively as the tube was rotated. A second ionization chamber receiving a portion of the direct beam was used in order to detect a possible variation of intensity of the incident radiation due to improper alignment and fluctuations of the current through the tube. When a zirconium filter, which is relatively transparent to the alpha lines, was used; it was found that the ratio of the intensity of radiation scattered parallel to the cathode stream to that scattered at right angles to the cathode stream was about 0.74. On using a strontium filter, which strongly absorbs the alpha lines, this ratio was about 0.84. One concludes from these results that the alpha lines are at least partially polarized.

12. An electron lattice theory of metals. Bertram E. Warren, Massachusetts Institute of Technology.—Metallic crystals are built up of positive ions and of electrons, both the ions and the electrons arranging themselves in a definite space lattice. The particular type of lattice utilized must represent a minimum of potential energy, and therefore depends on the number of valence electrons given up by each atom. The heuristic rule is laid down that atoms with one or two valence electrons will lose them, while atoms with more than two will lose only those in excess of two. The metals of Group I and III should utilize a complete lattice of the rock salt type, the sub-lattice of the positive ions being face centered cubic. In exception to this, the sub-lattice of the alkalies must be considered as face centered tetragonal. The sub-lattice of the metals of Groups II and IV should be either face centered cubic or hexagonal close packed. Groups V and VI should utilize a sub-lattice of the body centered cubic type. The lattice of a Group VII metal should not be of any of the simple types. These predictions are in very good agreement with the results of x-ray determinations. Such physical properties as the good ductility and conductivity of the face centered metals, and the high melting points of the body centered metals would be expected. The metals of Group VIII have not been classified.

13. The carbon atom model and the structure of the diamond. R. B. LINDSAY, Yale University.—Using a method similar to one previously described by the writer the 2_1 orbits in neutral carbon are approximately computed, introducing the assumption that the four orbital planes are arranged in tetrahedral symmetry. The atoms are then distributed in the diamond lattice and the field on any electron due to its own atom and neighboring atoms is calculated as a function of the distance from the nucleus assuming that: (1) the orbital plane of the electron is oriented in a certain symmetrical way relative to the lines joining its nucleus to those of the neighboring atoms; (2) for a first approximation only the four nearest atoms may be considered as effective; (3) the effect of the electrons in the neighboring atoms is that due to a time distribution of their charges in their orbital planes, disregarding definite phase relations such as have been assumed by previous writers. An approximate expression for the increase in energy of the electron orbit due to the neighboring atoms is developed, and the calculation of the lattice energy per electron for various values of a, the lattice constant, is carried out. The equilibrium value of a comes out between 1.10A and 1.60A (nearer the latter). In fact the heat of sublimation for $a=1.50$A is found to be 161 calories per mol. The accepted experimental values for these quantities are $a=1.54$A and $Y=168$ to 177 calories per mol. Compressibility calculations for this model are being undertaken.

14. The crystal structure of zirconium oxide. WHEELER P. DAVEY, General Electric Company.—ZrO_2 appears to crystallize in several forms. Using the powder method, diffraction patterns of two of these have been interpreted. One type shows that ZrO_2 may exist in a face-centered cubic lattice of ZrO_2, $a=5.098$A. The strong lines of the pattern taken alone show a diamond cubic pattern, indicating that the Zr^{++++} and 2 O^{--} are situated in the lattice like Ca^{++} and 2 F^{-} in CaF_2. The second type of diffraction pattern shows that ZrO_2 may exist in a triangular close-packed lattice of ZrO_2, $a=3.598$ and $C=1.633$. This structure is closely related to the face-centered cube. Both structures give a density of 6.13 which is to be compared with 5.75 given in 1860 by Nordenskiold.

15. Nickel-chromium solid solutions. F. C. BLAKE and A. E. FOCKE, Ohio State University.—A complete series of nichrome alloys has been studied by the powder method of x-ray analysis and the amount of distortion of the nickel lattice by chromium substitution and of the chromium lattice by nickel substitution has been determined.

The influence of impurity due to the crucible in which the melt is made has been studied and the correct lattices free from such influence have been determined. Intermetallic compounds and allotropic forms have been the subject of special study.

16. The ultra and extra-ultraviolet spectrum of iron as developed by the inverse photo-electric effect. OTTO STUHLMAN, JR., University of North Carolina.—A three element vacuum tube of the commercial form VT-I, with p'atinum filament and iron grid and plate, was used. In series with the grid was a sensitive galvanometer and a variable potential whose negative terminal was connected to the negative end of the filament. A second circuit with the positive end of a battery connected to the plate and its negative terminal connected to the galvanometer served to keep the plate at a constant positive potential higher than the positive potential of the grid. As a result of critically accelerating electrons, emitted by the filament, towards the grid monochromatic radiations are emitted, which are reabsorbed by the grid resulting in photoelectric emission. Such emission and absorption interpretations are given the discontinuities which appear in the potential-current curves. They are evaluated by the usual $V\lambda = 12344$ relation. Using a work function for iron equal to 5.000 volts the following spectral regions were reproduced. Spark spectrum of iron (Exner-Haschek, Spectren Tabellen) pronounced lines between 2456 and 2213. New lines between 2211 and 2154. Millikan, Bowen and Sawyer's spark spectrum, including the spectral region investigated by Bloch, from 2152 to 880A. The spectrum is being extended beyond 200A.

17. The extreme ultra-violet spectrum of titanium. R. C. GIBBS, Cornell University.—Using one of the vacuum spectrographs at the Norman Bridge Laboratory of Physics, California Institute of Technology, photographs of the hotspark spectrum of titanium were obtained over the region from 192 to 1718A. By comparison with the data of previous workers in this part of the spectrum, it was possible to identify many of the lines obtained on the plates as due to other elements such as oxygen, carbon and silicon, many of which are present with every element used as electrodes. By placing a plate for titanium and one for some other element obtained with the same setting of the spectrograph face to face on the comparator it was possible to determine with considerable accuracy, by taking relative intensities and structure of line also into consideration, what lines were not due to titanium. All of the twenty-five lines reported within the above limits by Lang were found and about ninety additional lines. Careful focussing and the use of a very narrow slit made it possible to fix the wave-length to within .05A in the case of many lines obtained in the second order. On one plate it was possible to observe in the second order all seven components of the 834 oxygen line.

18. On the spectrum of argon. F. A. SAUNDERS, Harvard University.—The spectrum of argon in the extreme ultraviolet obtained by T. Lyman shows a very strong pair at $\lambda\lambda 1048.26$ and 1066.72, and many other lines, some as yet unidentified. Following Paschen's neon notation, this pair is a combination between a $1p$ level $(j=0)$ and $2s_2$, $2s_4$. The known frequency-differences in the rest of the argon spectrum yield the terms $2s_3$ and $2s_5$, and many $2p$ terms are readily obtained, some of which combine with all four s terms, others with s_2, s_4 and s_5 only, as in neon. Three of the latter (presumably p_4, p_6 and p_8) are unexpectedly found to combine with $1p$, and produce strong lines ($\lambda\lambda 941.39$, 932.09, 919.80). The same combinations also produce lines, (though weaker) in neon ($\lambda\lambda$, 662.84; 665.30; 667.46), not previously identified. For these lines j must change from 0 to 2; they are thus quite unconventional. They are produced with a mild excitation. Other pp combinations seem to be present, but are not yet firmly established (e.g. Argon $\lambda 946.95$). Many other terms in the argon spectrum have also been found, and photographs have been taken in the ultrared, which are yielding data for a complete analysis of this spectrum.

19. The quantum theory of the Zeeman effect for band lines. E. C. KEMBLE, Harvard University.—Assuming an electronic angular momentum with fixed components σ and ϵ along and perpendicular to the axis of figure of a diatomic molecule, the application of Bohr's postulates to the precessional motion in a magnetic field leads to the Zeeman term formula

$$E=E_0+rh\Delta\nu_n(\sigma^2+\epsilon(j^2-\sigma^2)^{\frac{1}{2}})/j^2,$$

where r is the magnetic quantum number, subject to the usual selection principle, $\Delta\nu_n$ is the Larmor frequency. j is the total angular momentum. The following qualitative inferences may be drawn: (a) The Zeeman pattern for lines adjacent to a band origin will normally be simple and the scale may be similar to that for an atomic line. (b) The outer lines of a band will have very complicated patterns, usually on a scale entirely too small to detect. (c) If the initial and final values of ϵ are different, the outer lines of a band will seem to be diffusely broadened in a magnetic field. (d) The direction of rotation for the Faraday effect in the neighborhood of a band line will frequently be different for the P and R branches of the same band. The theory agrees with the meagre experimental facts only in general qualitative features.

20. On the continuous spectrum of hydrogen. W. H. Crew and E. O. Hulburt, Naval Research Laboratory, Washington, D. C.—In a discharge tube filled with dry hydrogen at a moderate pressure (1 to 3 mm Crookes dark space) the striations near the negative end of the positive column have quite different colors, widths and spacing; the first is a vivid blue and narrow, the second or third is pinker and wider, the third or fourth bluer again, the remainder being pinker or whiter for the most part. Spectrograms showed that the first blue striation, i.e. the one next to the Faraday dark space, emitted the continuous spectrum of hydrogen in great purity, the Balmer and molecular lines being relatively feeble. In the other striations the continuous spectrum was weaker than the line spectra, and in the cathode glow, Crookes dark space, negative glow and Faraday dark space was absent. The intensity decrement of the Balmer lines appeared to vary in different parts of the discharge. With moist hydrogen the Balmer lines were bright and the continuous spectrum dim in the striations. These facts together with the positive the ray analyses of the ions in a hydrogen discharge by Smyth and Brasefield support the conclusion that H_3 is the source of the continuous spectrum of hydrogen.

21. The structure of the hydrogen molecule. H. C. Urey, Johns Hopkins University.—Recently Dieke and also Takahashi have arranged the Fulcher bands of hydrogen into single band systems with each band consisting of a zero branch. To these Dieke has added positive branches for the red bands and incomplete branches for the green bands. A study of these positive branches shows that they may be rather doubtful. Witmer has shown that the Lyman bands in the far ultraviolet have a similar structure. Since only one band system appears in each group it seems most reasonable to assume that the vibration quantum number does not change in these transitions and that therefore the molecule is symmetrical about the median plane. Since the bands have only zero branches the molecule must have no angular momentum in the electron system for otherwise the frequency of rotation of the nuclei would appear in the Fourier expansion of the electron motion and therefore positive and negative branches would appear. It seems necessary to assign the steady states involved to the *vibration* electron orbits of the median plane. This would give no first order Zeeman effect as required and a diamagnetic model for the normal state.

22. The structure of the hydrogen molecule ion. H. C. Urey, The Johns Hopkins University.—The energy levels of the vibrational model of the hydrogen molecule ion have been calculated including the energy contributed by the vibration and rotation of the nuclei. The calculated spectroscopic term is

$$\nu=-134899/n^{*2}-9.37/n^{*4}+5358n_4/n^{*3}+107.6m_1^2/n^{*4}-0.1767m_1^4/n^{*6},$$

where n^*, n_4, and m_1 are the quantum numbers conjugate to the electron coordinate, and the vibrational and rotational coordinates of the nuclei respectively. The application of the correspondence principle to the model requires that $\Delta n^* = 1, 3, 5, \ldots,$ $\Delta n_4 = 0$ and $\Delta m_1 = 0$ for transitions emitting light. Bands emitted from such a molecule should consist of single band systems, each band having a zero branch only. Exact agreement between theory and experiment has not been found.

23. **P, Q, R combinations in the sodium hydride many-lined molecular spectrum.** E. H. Johnson, University of Chicago.—A study has been made of the many-lined spectrum obtained from sodium arc in hydrogen in the region from λ5500 down to λ3800. Direct comparison of high dispersion plates shows an arrangement wholly different from that of the hydrogen secondary spectrum. Though at first sight there is little evidence of band structure, several groups of P, Q and R branches have been traced out by means of the combination principle. The $\Delta F(m)$ relations indicate the presence of a Kramers and Pauli effect. Preliminary values of $2B$ lead to a final moment of inertia of about 5.5×10^{-40} gm cm^2, which gives a nuclear separation of about 1.8×10^{-8} cm for a sodium hydride dipole. A detailed quantum analysis of the bands is included.

24. **Half-integral vibrational quantum numbers and rotational energy data for the MgH bands.** William W. Watson, University of Chicago.—The magnitude of the isotope effect in the λ5211 band is shown to agree exactly with the assumption that $n' = \frac{1}{2}$ and $n'' = \frac{1}{2}$ as demanded by the new quantum mechanics. The "zero-points" of this band system can be represented by the equation

$$\nu = 19217 + (1603.5\ n' - 34.75\ n'^2) - (1493.5\ n'' - 31.25\ n''^2)$$

where n' and n'' take on half-integral values from $\frac{1}{2}$ to $3\frac{1}{2}$. For the final state in the λ5211 band, the rotational energy can be represented by $F = Bm^2 + Dm^4 + Fm^6$ where $m = j + \frac{1}{2} - \epsilon$, ϵ having the approximate value 0.47. Kemble's formula, $\omega = (-4\ B^3/D)^{\frac{1}{2}}$ gives the vibrational frequencies in the ν_0 formula to within the experimental accuracy of the data. The values of ΔF for the initial state indicate the presence of a Kramers and Pauli effect. The results of a least square solution and the question of missing lines lead to the approximate value $\epsilon = 0.43$ for the initial state. A comparison with rotational energy data for the C+H bands is made.

25. **Nitrogen Series in the ultraviolet.** J. J. Hopfield, University of California. —Four new series, namely, two series of triplets probably converging to a common head and belonging to the quartet system, and two series of doublets also having a common limit and belonging to the doublet system, have been observed in nitrogen. The short wave-length lines of one of the triplet series are given accurately by the equation

$$\nu = 117353 - 109677(m + 0.845685 - 0.022749/m^2 - 0.026562/m^4)^{-2}$$

in which $m = 1$, 3 and 4 correspond to terms already observed by Kiess. $m = 2$ gives a new triple term, and $1S = 117353$ (14.48 volts) is the lowest energy level yet observed in neutral nitrogen. The two doublet series which begin with the previously known lines at λ1742 and λ1592 respectively have each been observed to three members. Their common limit is 98100 cm^{-1} (12.11 volts). The terms representing these series are linked to the doublet terms already observed through the lines at λ1742. The resonance and ionizing potentials of neutral nitrogen are contained in the data given above. Inter-series and other relations are now being studied.

26. **The infrared spectra of brucite and some sulphates; isotopic effect.** E. K. Plyler, University of North Carolina.—By means of an infrared spectrometer the structure of the absorption band of brucite [$Mg(OH)_2$] was studied. The region of greatest absorption was found to be at 2.48 μ. Besides this maximum there were small maxima of absorption located at 2.40 μ, 2.30 μ, 2.14 μ. The maxima at 2.48 μ, 2.40 μ, and 2.30 μ correspond approximately in position and absorption to the isotopes of Mg^{24}, Mg^{25},

and Mg^{26} as found by Aston. The small band at 2.14 μ, corresponds in position to Mg^{28}. However this isotope is not given. The work of Coblentz has been examined for the isotopic effect. In the reflection spectrum of nickel sulphate in solution there are two maxima located at 9.15 μ, and 9.50 μ. The second is more intense. These maxima are probably due to Ni^{58} and Ni^{60}. In the spectrum of potassium sulphate there are two maxima, one at 9.00 μ, and the other at 9.40 μ. The maxima at 9.40 μ is much more intense. These two maxima are probably due to K^{39+41} and K^{39} taken twice. Other sulphates in solution only showed one maximum.

27. **The intensities of the lines in the HCl absorption band at 3.5μ.** D. G. Bourgin and E. C. Kemble, Harvard University.—Measurements of the absorption curves for the HCl band at 3.5 μ have been made by the writers with tube-lengths varying between 0.1 cm and 3 cm. From plots of the areas of the individual lines against tube-length the areas of the corresponding absorption coefficient curves have been determined. The measurements cover all lines between the tenth of the R branch and the sixth of the P branch. The results are in harmony with the formula previously derived by one of us (Phys. Rev. **25**, 1, (1925)) provided that the statistical weight series 1, 3, 5, 7, . . . is used as suggested by Fowler and Dieke (summation rule). The agreement between the results and the theory was within three percent of the intensity of the strongest line for all but two of the lines measured. From the shapes of the area-tube-length curves it may be inferred that the lines are very sharp, the center of the strongest lines being completely absorbed in the first few millimeters of absorption path. The variation in the shapes of the curves from line to line shows definite evidence of a rotational isotope effect.

28. **Analysis of Wood's iodine resonance spectrum.** E. C. Kemble and E. E. Witmer, Harvard University.—The resonance spectrum of I_2 excited by the broadened green mercury line consists of several series of doublets. According to Lenz each doublet is due to molecular transitions from a definite initial excited state to two different final rotational states. The different doublets in a series are due to different final vibrational states, the different series to a variety of initial states present because the exciting line covers a number of absorption lines coming from different absorption bands. Mecke has partially analysed some of the absorption bands in the red and has worked out empirical formulas for the frequencies of the resonance series. Kratzer and Sudholt have written out theoretical formulas for the resonance series in harmony with the observations and from Mecke's data have evaluated the moment of inertia of the molecule. Assuming that the nuclear rotational quantum numbers of the final states associated with each doublet differ by exactly two, the authors have revised and extended the work of Kratzer and Sudholt. We obtain the values 7.9×10^{-38} gm cm^2 and 11×10^{-38} gm cm^2 for the moments of inertia in the normal and excited states respectively. The large difference between these values locates the origin within three lines of the head.

29. **The fluorescent and absorption spectra of iodine.** F. W. Loomis, New York University.—The four series without linear terms found by Mecke (Ann. d. Phys. **71**, 104, (1923)) in Wood's spectrum of fluorescent iodine excited by the broad green mercury line are due to four lines of the band (26, 0); those with positive doublet interval to lines in the P branch. The P and R branches are the absorption series Ia and Ib found by Mecke in this region. The fluorescent lines are identified. This makes it posisble to pick out a series of pairs of lines with common m', and another with common m'' and hence to find $B_0''=0.03835$, $B'=0.02480$ cm^{-1}, $J_0=(7.21\pm.03)\times10^{-38}$ and the absolute values of m which turn out half-integral. Similarly, lines of Mecke's series II belong alternately to the P and R branches of band (27, 0) and the fluorescent lines are identified as are also the main lines in three of the four remaining fluorescent series. Wood's measurements of the magnetic rotation of six absorption lines show in every case the

"normal" direction of rotation for lines here assigned to a P branch and the opposite for R lines. These results demonstrate the existence of P and R branches in absorption, which Mecke has doubted, and confirm the Lenz theory.

30. On the polarization of fluorescent light from colloid solutions. PAUL FRÖHLICH, University of Chicago, (introduced by William W. Watson).—The partial polarization of fluorescent light from aqueous solutions of fluorescein, eosine, magdala-red, rhodamine 5 G, and rhodamine B extra, produced by dissolving in them more and more gelatine, gum arabic, or agar-agar; and in acetone solutions of the same substances by dissolving in them successively more celluloid, has been investigated. Three different wave-lengths of the plane polarized exciting light were used. It is found that the percent of polarization is successively increased from zero or a low value to a maximum, by dissolving in the solution a colloid. The maximum value will be reached in some cases with 60 percent, in others with 100 percent colloid in a solid film. The percent of polarization in the case of colloid solutions shows the same effects as in the case of non-colloid solutions with a high viscosity, such as glycerin or oils. It is increased by lower concentration of the dye, and by longer exciting wave-length. With dyes having shorter wave-length absorption bands (fluorescin, eosine), the wave-length effect proceeds at a slower rate than with solutions having longer wave-length absorption bands (magdala-red, rhodamine). By suitable choice of concentration and exciting wave-length, the maximum value of the polarization is about 35 to 40 percent.

31. Fluorescent exciting power and black-body radiation. E. H. KENNARD, Cornell University.—Suppose one quantum number n of an atom has normally the value n_1 while another m is statistically distributed by thermal agitation. Let absorption at frequency ν_x change n to n_2 and m from m_1 to m_2; and suppose that after this process thermal agitation is either (a) ineffective (then $m_2=m_3$ below) or (b) completely effective in re-distributing m statistically. Suppose fluorescent emission of frequency ν_y then occurs while n changes back to n_1 and m changes from m_3 to m_4. Then the Einstein theory (1917) leads to the equations

$$\phi_{yx}=k_x\alpha_y u_y, \qquad \phi_{yx}/\phi_{xy}=\nu_y u_y/\nu_x u_x,$$

where ϕ_{yx}=fluorescent emission of frequency ν_y per unit volume excited by unit energy density at ν_x, α_y=absorption coefficient and u_y=black-body density of radiation for ν_y, and the factor k_x depends on ν_x but not on ν_y. These equations should hold for iodine fluorescence, n referring to the electron jump and m either to the rotation of the molecule or to the atomic vibration. For the second equation, restrictions (a) and (b) are probably unnecessary. Perhaps the equations will hold also for fluorescent solids and liquids; experiments are in progress.

32. Transformation spectra and the principle of essential indentity. E. L. NICHOLS and H. L. HOWES, Cornell University.—At their transformation points many incandescent bodies, particularly certain oxides, emit light over and above that due to their thermal state. The effect, although reversible, is most readily seen as a temporary flash up when a small mass of the substance is cooling. Through the spectroscope it may be seen to be selective. When the incandescent body contains a rare earth in solution, as activator, the *transformation spectrum* consists of narrow bands which appear suddenly in the field of view and melt away as the temperature falls below the transformation point. *These coincide with the fluorescence bands characteristic of the activator* or where that is not the case are members of the sets of equidistant components of which the fluorescence spectrum is composed. In other words, the fluorescence spectrum and transformation spectrum for a given activator are essentially identical and the principle of *essential identity*, hitherto applied to luminescence at ordinary temperatures is extended also to the luminescence of incandescent substances. (Nichols and Howes, Phys. Rev. **19**, 304 (1922).)

33. The form of the absorption bands in solutions of the organic dyes, and a relation between absorption and fluorescence. ERNEST MERRITT, Cornell University—It is assumed that the active molecule behaves as an electric doublet whose moment changes from μ_0 in the normal state to μ_1 when excited. In the field E due to the solute molecules the frequency for absorption, or emission, is then ν instead of ν_0, where $h\nu = h\nu_0 + (\mu_1 - \mu_0)E$. If thermal equilibrium is assumed the absorption coefficient α, which is determined by the distribution of the normal molecules, and the fluorescence F, determined by the distribution of the excited molecules, will be

$$\alpha = V(E)\exp(-\mu_0 h(\nu-\nu_0)/kt(\mu_1-\mu_0)), \quad F = F_0 h\nu V(E)\exp(-\mu_1 h(\nu-\nu_0)/kt(\mu_1-\mu_0)),$$
$$F/\alpha = F_0 h\nu \exp(-h(\nu-\nu_0)/kt),$$

where $V(E)$ is the volume within which the field (in the direction of μ_0) lies between E and $E+dE$, and F_0 depends on the duration of the excited state. If the solvent molecule is also a doublet, $V(E)$ is shown to be independent of ν through a considerable range, so that α is exponential on the long wave side of the band. This result is confirmed by experiment with uranine in water. Measurements, not yet of high accuracy, indicate agreement with the theory to within 10 percent in the value of F/α.

34. Gyromagnetic electrons and a classical theory of atomic structure and radiation. LOUIS VESSOT KING, F.R.S., McGill University.—A charged sphere in rotation with spin Ω_1 is deformed by translational velocity v into an ellipsoid of revolution, and as a result acquires the properties of a gyrostat in so far as precessional oscillations are concerned. The electrodynamic coefficients of inertia (A, C, C) are rigorously determined by integrating the magnetic energy throughout the space, within and without the ellipsoid whose deformation is considered to be physically real. It is shown that the frequency ν of precessional oscillation is given by

$$2\pi\nu = \Omega_1(C-A)/C = \Omega_1(c_1-a_1)\beta^2(1+b_1\beta^2+b_2\beta^4+\ \ldots\ ), \tag{1}$$

and leads to the formula $h\nu = \frac{1}{2}m_0 v^2$(2)for moderate velocities, where $m_0 = \frac{2}{3}e^2/a$ and $\beta = v/c$, the velocity of light being denoted by c. Remembering that a precessing electron has the properties of a small magnet, and therefore can radiate electromagnetically, equation (2) is the well-known photo-electric equation, while h becomes a fundamental constant of a rotating electron expressed in terms of spin by the relation $h\Omega_1 = \pi c^2 m_0/(c_1-a_1)$(3) where (c_1-a_1) is a numerical constant equal to $\frac{2}{5}$ for the simple model considered. The spinning deformed electron leading to equation (2) appears to give, on classical mechanics and electrodynamics, the key to radiation problems generally, and in the corresponding theory of atomic orbits yields the principal fundamental series formulae, as well as an adequate account of fine structure, Zeeman and Stark effects.

35. Light quanta and interference. A. J. DEMPSTER, University of Chicago. Experiments by W. Wien and by the author have shown that after 5×10^{-8} seconds the process of light emission from a radiating atom is practically complete. The energy from a glow discharge radiated in the helium line 4471 (decay constant 5.42×10^7) was measured by comparison with the intensity of the spectrum from a black body at a known temperature. The glow discharge was made so faint that 8.4×10^{-11} ergs or 19 quanta fell on the end of an echelon diffraction grating per second. With this intensity each light quantum must pass through the echelon separately. Interference patterns were photographed, showing the same appearance as with bright sources. In particular the characteristic double order image was photographed, indicating interference of rays that have passed simultaneously through the fifteen different steps of the echelon.

36. Effect of an electric field on the radiation from hydrogen atoms. K. L. HERTEL, University of Chicago. (Introduced by A. J. Dempster).—Canal rays were allowed to pass from a discharge tube through a small hole into an observation chamber which was kept at a very low pressure (.0005 mm of mercury). The luminosity from the rays died out rapidly as found by other observers. The light from the canal rays on first entering the low pressure chamber was observed to be partially polarized, the component parallel to the bundle being the stronger. It was found that the polarization decreased with increasing distance from the opening, the rate of decrease of the polarization being greater than the rate of decrease of the intensity of the rays. When an electric field was applied across the bundle the polarization observed at right angles to the field behaved quite differently. The initial polarization altered very rapidly, and, at two millimeters beyond the opening, was reversed so that the component polarized parallel to the bundle was weaker than the other. This partial polarization then gradually decreased in the field at about the same rate as a polarization then gradually decreased in the field at about the same rate as a polarization observed without the electric field.

37. The effect of changing the conditions of excitation upon the time of appearance of certain spark lines of cadmium and zinc. J. W. Beams, National Research Fellow, University of Virginia.—The appearance of the spark lines of cadmium and zinc was studied in the two spectra produced when the same spark discharge passed between metallic electrodes in air and through the ionized vapor of the metallic arc, by a method previously described (Brown and Beams, J.O.S.A. & R.S.I., **11,** 11, (1925)). Each of the spark lines 4924, 4912 $(4d_{1,2}-4f)$; 6103, 6021 $(4p_1-5d_1)$, $(4p_2-5d_2)$ of zinc and 5378, 5338 $(5d_1-4f_1)$, $(5d_2-4f_2)$ of cadmium were observed to appear simultaneously in both spectra. From this it is concluded that the sequence in the appearance of spectrum lines in the spark is predominantly an atomic phenomenon and practically independent of the characteristics of the spark discharge.

38. Intensities in spectra and the new quantum mechanics. Frank C. Hoyt, National Research Fellow, University of Chicago.—On the basis of the new quantum mechanics of Heisenberg and Born it becomes possible for the first time to obtain exact expressions for the intensities of spectral lines. If the intensities for the linear oscillator as given by Born (Zeit. f. Phys. **34,** 858 (1925)) are compared with those calculated on the basis of the older form of the theory it is seen that no one of the possible expressions which were previously proposed can be regarded as exact, provided the new theory is accepted. Computations from the new theory are shown to be in agreement with the relative intensities of the (01) and (02) bands in HCl.

39. The use of a cathode-ray tube for the transmission of speech. C. W. van der Merwe, Washington Square College, New York University, (Introduced by H. H. Sheldon).—One of the chief defects of the "speaking arc" as used by H. Th. Simon in 1898 was its comparative failure to reproduce in a satisfactory manner high-pitched tones. This failure was obviously due to the thermal inertia of the arc. The minuteness of the mass of the electron, and for that matter of the atom, suggested the substitution of an ordinary discharge tube for the electric arc. A tube of special construction containing a trace of a mixture of helium and neon was used and the substitution met with marked success, the high notes coming through much more clearly than in the case of the arc, sibilants like "s" and "c" being distinguishable from one another and voices being recognizable. Quantitative comparisons confirmed the superiority of the tube over the arc, and with a current of only 10 milliamperes flowing through the former, it was possible to telephone a distance of 60 feet with the greatest ease. The key to the success of the "speaking tube" is the luminosity of the discharge, since the light from the glow has to be reflected to the receiver. The success of this essentially wireless telephone will therefore depend on the efficiency with which discharge tubes carrying large currents can be built.

40. Experiments on cathode sputtering. E. O. Hulburt, Naval Research Laboratory, Washington, D. C.—Experiments with the flying metallic particles sputtered from a cathode have yielded the following facts. The side of a glass plate away from the cathode receives a film of metal as well as the near side. There is no critical relation between the position of the glass plate with reference to the boundary of the cathode (Crookes) dark space and the film received. Shadows on the metallic film, in some cases geometrical and in others more complex, are cast by diaphragms and obstacles. No evidence of the reflection of the particles from glass or metal plates was obtainable. The particles enter open-ended glass tubes only to a distance roughly equal to the diameter of the tube. Some of the particles leave the cathode surface normally and therefore may be focussed on to a glass plate by a concave (spheridal surface) cathode. The circular film thus formed, however, had an unexpected hole in the center. Likewise a cylindrical cathode, which should concentrate the film into a strip, did so, but the strip had a central line of no deposit. The explanation of the various effects is perhaps to be found in the different sizes, velocities and charges of the flying particles combined with the many complexities of the interior of a discharge tube. Experiments with twenty-two metals enable them to be classed according to their relative ease of sputtering.

41. Normal arc characteristic curves depend on the absolute temperature of the anode. W. B. NOTTINGHAM, Princeton University.—The characteristic curves for normal arcs in air have been found to follow $V=A+B/I^n$ where V is the potential drop, I the arc current, A, B, and n constants with n directly proportional to the temperature of the boiling point of the anode material. Since the publication of this equation (Trans. A.I.E.E. Jan. 1923, p. 12) it has been verified by Anderson and Kretchmar (Phys. Rev., **26**, 33, (1925)) for short platinum and tungsten arcs of small current intensity. Recent measurements on tungsten arcs 2.0 mm to 10.0 mm in length and for currents 1.0 to 10.0 amperes show the average value of n to be 1.38 indicating a temperature of 5250°K while for the six arc characteristics of lengths between 5.0 mm and 10.0 mm the value of n was found to be 1.34 which corresponds to a temperature of 5100°K and agrees exactly with the Langmuir calculation. (Phys. Zeit., **14**, 1273, (1913)). The ten points now located along the straight line $n=2.62(10)^{-4}T$ are

Anode	W	Pt	C	CuO	Al_2O_3	NiO	Ag	Pb	Sb	Bi
T° K	5100	4180	3770	2580	2480	2450	2370	1850	1710	1690
n	1.34	1.15	0.985	0.67	0.65	0.64	0.624	0.48	0.46	0.445

These observations indicate that there may be something more significant to the equation $V=A+B/I^n$ than simply a convenient empirical formula and should be recognized as an experimental fact to be explained by any comprehensive theory of the electric arc.

42. Collisions between electrons and gas molecules. IRVING LANGMUIR and H. A. JONES, General Electric Co.—By a method already described (Science, **59**, 380 (1924)) the volt-ampere characteristic of a cylinder surrounding a coaxial cathode in a gas at low pressure gives quantitatively the probability P (per cm of electron path) that the electron, of 50 to 250 volt energy, will make a collision of a specified type. Thus the collisions may be elastic (P_e) or inelastic (P_k) and the inelastic collisions include those that ionize (P_i) and those (P_r) that make the electron lose a definite energy corresponding to a resonance potential (E_r volts). The electrons that make elastic and resonance collisions are scattered by each such collision only through small angles distributed according to probability laws, θ_e and θ_r being $2/\pi^{\frac{1}{2}}$ times the most probable angle of deflection in degrees. The results for 100 volt electrons calculated for a gas pressure of 1000 bars at 20°C are

Gas	P_e	P_k	P_r	θ_e	θ_r	E_r
Hg	19.	33.	10.	14	14	6.7
A	10.	14.	1.3	14	14	13.
He	1.4	2.7	0.9	26	20	20.
N_2	7.8	12.2	3.6	14	18	13.
H_2	4.8	7.1	2.8	14	15	12.

43. Collector characteristics in neon and helium. R. RUDY, Nela Research Laboratory.—After having passed for variable distances through neon at pressures from .01 to 1 mm Hg, 70-volt electrons were received upon a disk. With a retarding field of over 100 volts, only positive ions reached the filament; their number remained nearly unchanged as the collector was moved away for a distance of several cms, and then started to decrease. When the collector was given the potential of the cathode, it began to receive primary electrons, which caused a break in the characteristic. From the slope, their average energy could be determined for different positions of the collector and compared with the results deduced from the theory of the scattering of electrons. Even in inert gases, the loss of energy is considerable besides excitation and ionization, whereas it is often neglected in the work on activation and disappearance of gases in the electric discharge. As the pressure was increased, the break disappeared entirely; the collector was now in the "positive column" of the discharge; a strong increase in current occurred only when the anode potential was approached. With heavier discharge currents space charges (e.g. near the collector) disturbed the field and discontinuous changes were noted.

44. Hydrogenation of ethylene by excited mercury atoms. A. R. OLSON and C. H. MEYERS, University of California.—In a previous article, (J. A. C. S. **48,** 389 (1926)), we have shown that ethylene and hydrogen react to form ethane under the influence of excited mercury atoms. The rate of the reaction was found to be proportional to the square root of the partial pressure of molecular hydrogen when all other factors are kept constant, and therefore the primary reaction is $H_2=2H$. The atomic hydrogen then diffuses from the illuminated region into the body of the gaseous mixture where hydrogenation occurs. The addition of an inert gas such as nitrogen should lower the diffusion rate. This effect is in qualitative agreement with the increased brightness of the thallium lines in the presence of nitrogen as observed by Loria, and in the decreased reaction rate of water formation from oxygen and hydrogen in the presence of nitrogen as observed by Mitchell. In the present set of experiments a gaseous mixture composed of 2.5 mm of N_2, 4.5 mm of H_2 and 1.2 mm of C_2H_4 were circulated past the illuminated window. The rate of reaction was found to be the same, within experimental limits, as the rate for the same mixture without the nitrogen. Under these conditions any increase of reaction rate due to metastable mercury atoms, must be offset by a decrease of rate due to diffusion. The broadening of the absorption line of mercury due to the added nitrogen was investigated by an external filter containing mercury vapor and found to be negligible.

45. Measurement of the increase of metastable atoms in mercury with accelerating voltage. HELEN A. MESSENGER and HAROLD W. WEBB, Columbia University.—The "radiation" from mercury vapor excited in a four-electrode tube by electrons from an equipotential cathode was measured by the "photo-electric" current from the nickel plate which was not sensitive to λ2537 radiation. A quartz or a calcite window could be lowered at will into the space between the grids to cut off metastable atoms from the plate. With no window typical Frank and Einsporn curves were obtained showing all the breaks which they found. With quartz a similar curve was obtained above 5.2 volts although the current was reduced to 10% or less. Below 5.2 volts there was no measurable current. With calcite the currents were still smaller; the 5.7, 6.7, 8.05 and 8.35 breaks were missing. The difference between the "photo-electric" currents in the open tube and those obtained with quartz interposed measures the increase of metastable atoms with accelerating voltage. The difference between the quartz and the calcite curves shows the presence of λ2140 radiation and further shows that the λ1849 radiation increases linearly from 6.7 volts.

46. The formation of negative ions in mercury vapor. WALTER M. NIELSEN, Duke University.—The method used is similar to that of Mohler (Phys. Rev. **26,** 614, (1925)) Electrons, projected along the axis of a tube between two plates were prevented from scattering by a magnetic field of 350 gauss parallel to the axis of the tube. Negative ions formed by the attachment of an electron to a molecule or to an atom were removed by suitable potentials applied to the side plates. The remainder of the current reached a circular plate at the end of the tube. With a small field between the side plates, the negative ion current was just barely observable (1×10^{-10} amperes). With higher fields the ion current increased enormously, approaching saturation when the potential difference between the side plates was increased to between 3 and 4 volts. The negative ion current was of the order of 9×10^{-9} amperes. The total current was of the order of 1×10^{-7} amperes. The ratio between the negative ion and total current decreases with increase in the driving potential for low voltages, but increases at 2.7, 4.7, 5.5, and 8.8 volts. The cause of the break at 2.7 volts is not known. The breaks at 4.7, 5.5, and 8.8 volts are believed to be associated with the electronegative properties of the mercury atom having an electron in a metastable orbit. The total current increases rapidly with increase in the driving potential and decreases at 4.9 and 6.7 volts.

47. Resonance and ionization potentials in mercury vapor. C. W. JARVIS, Ohio Wesleyan University.—Measurements on the critical potentials in mercury vapor were made with two types of tubes: (1) a three-electrode tube by which both total and partial currents were observed; (2) Hertz differential tubes of several different sizes. The table shows the values obtained together with those calculated from the relation $Ve=h\nu$ and those reported by Franck and Einsporn.

Calc.	F. & E.	Author	Calc.	F. & E.	Author	Calc.	F. & E.	Author
1.26		1.23	5.28	5.32	5.22	7.69	7.73	7.74
2.26		2.21	5.43	5.47	5.37		8.05	8.02
2.83		2.80	5.73	5.76	5.70		8.35	8.33
3.37		3.44		6.04	6.05	8.81	8.86	8.82
3.70		3.80		6.30	6.46	9.32	9.37	9.33
4.16		4.21	6.67	6.73	6.79	9.52	9.60	9.58
4.66	4.68	4.53		7.12	7.13	9.80	9.78	9.90
4.86	4.90	4.97		7.46	7.41			

A number of critical potentials below 4.68 volts were observed. The interpretation of these is much in doubt, as they imply that in normal mercury vapor the valence electron is in a higher energy level than that corresponding to the ground orbit of the valence electron. Perhaps they may be attributed to the molecule of mercury.

48. The ionization potentials of hydrogen and nitrogen on an iron catalyst. GEORGE KISTIAKOWSKY, Princeton University, (Introduced by K. T. Compton).—By the method of electron bombardment, Gauger and Wolfenden showed that hydrogen adsorbed on nickel has radiation and ionization potentials characteristic of atomic hydrogen. Nitrogen adsorbed on a promoted iron catalyst has now been studied by an improved method. The catalyst was prepared by reduction in hydrogen and contained residual hydrogen. Ionization potentials in presence of nitrogen were found at 11.1, 13.0, 16.0, 17.1 corrected volts. The two highest doubtless belong to molecular hydrogen and nitrogen. 13.0 volts is slightly different from the ionization potential of gaseous atomic hydrogen, but evidently the energy required for ionization of an adsorbed gas atom is not necessarily the same as that for a free atom. This energy is compounded of the ionization energy of a free atom plus its adsorption energy minus the energy of adsorption of a free electron by the metal. The last two terms are not necessarily equal, though they are known for hydrogen to be not very different. The ionization at 11.1 volts was only observed when catalyst and nitrogen were both present and belongs, probably, to atomic nitrogen, whose gaseous ionization potential has been estimated spectroscopically as about 11 volts. Catalytic poisons were found to suppress the critical potentials at 11.1 and 13.0 volts.

49. Direct determination of the ratio of Planck's universal constant to the charge on the electron. Ernest O. Lawrence, National Research Fellow, Yale University.—The precision of the method for critical potential measurements described at the Montreal meeting has been developed to a greater degree. The most recent determinations of the ionization potential of Hg vapor with assigned "weights" are:

Volts	Weight	Volts	Weight
10.46	8	10.36	5
10.32	4	10.40	4
10.42	10	10.44	4
10.37	10	10.39	10

Calculating in the usual way the mean value and probable error we have for the ionization potential 10.399 (±.007) volts. Applying the quantum postulate to the series limit there results for the ratio h/e the value $1.3735\ (\pm .0009)\times 10^{-17}$. Using Millikan's determination of e we have for h the value $6.550\ (\pm .006)\times 10^{-27}$, in which the error presumably is concerned with the uncertainty in e. These results are tentative pending the outcome of a thorough investigation of possible sources of systematic error.

50. On the threshold sensitivity of photographic emulsions to low speed electrons. Kenneth Cole, Cornell University, (introduced by F. K. Richtmyer).—A new design of magnetic dispersion electron spectrograph has been used in an investigation of the sensitivity of photographic emulsions to electrons of speeds below 100 volts. With commercial emulsions, the lowest speed that will produce a perceptible effect depends upon the emulsion and is usually in the neighborhood of 30 volts. It has been found however that a very thin film of lubricating oil on the surface of the emulsion enormously increases its electron sensitivity and at the same time lowers the threshold speed. With both oiled and unoiled emulsions, the photographic action seems to be due to fluorescence excited at the surface by the electron impact.

51. Secondary emissions from metals due to bombardment by high speed positive ions. Wilfrid J. Jackson, Princeton University, (Introduced by K. T. Compton).—A beam of K^+ ions from the iron catalyst source discovered by Kunsman was collected in a Faraday cylinder. A target could be interposed at the mouth of the cylinder by a magnetic control. The difference in current measured in these two cases gave the amount of the secondary emission. A transverse magnetic field could be applied at the target to prevent emission of electrons and thus separate electron emission from positive ion reflection. On bombardment of a molybdenum target which had been baked in *vacuo* to 1000°C and then exposed to air before final evacuation of the apparatus, secondary emission was inappreciable if the energy of the bombarding ions was less than 250 volts, was appreciable (1%) at 350 volts and rose steadily to about 9% at 1000 volts. These values depended somewhat on previous treatment of the target. After heating in position in vacuo by induced currents the emission fell to not more than a third of the above values. The secondary electrons were stopped by retarding fields of 0.25 volts. Positive ion reflection did not exceed 2%. Secondary emission from nickel was first detected at about 400 volts and increased to about 7% at 1000 volts.

52. Long wave length limit of mercury. Wayne B. Hales, California Institute of Technology.—Kazda made the first definite and satisfactory determination of the critical potential and long wave-length limit for a clean flowing merucry surface, locating this critical frequency at 2735A with an uncertainty of ±10A. Sophie Taubes' recent determination made on mercury drops suspended in argon was very much higher, namely, 3043±20A. I have, with completely new apparatus and new working conditions, found this long wave-length limit to be 2735A and have succeeded in getting a stationary surface so clean that the critical frequency has been found for it, namely, 2735±10A which is in entire agreement with Kazda for flowing mercury.

53. A new effect in the photo-electric emission from oxide-coated filaments. W. H. Crew, Naval Research Laboratory, Washington, D. C.—Total radiation from a quartz mercury arc was directed on to the oxide-coated platinum filament of a two-electrode quartz vacuum tube. Current-voltage curves were obtained with and without the light shining in the tube; and from these was determined the electron current due to the light alone. This current, plotted as a function of the plate voltage, increased rapidly to a maximum and thereafter fell off gradually. The position of this maximum was found to shift in the direction of decreasing potentials with increase of the temperature of the filament. Similar phenomena were observed with a filament made of oxide-coated tungsten, but could not be detected for either platinum or tungsten without oxide coating. The photo-electric emission was largely due to light of wave-length below λ3000A; for the photo-current was reduced almost to nothing by use of suitable glass absorbing screens, and was enhanced when mercury vapor was removed from the tube and the arc was water-cooled. The explanation of these phenomena is perhaps to be found in the changes in the surface of the filament under the action of the light rather than to space-charge effects.

54. The theory of thermionics. N. Rashevsky, Westinghouse Elec. & Mfg. Co., East Pittsburgh, (introduced by Dayton Ulrey).—The expression for the free energy of a metal is derived by computing the "Zustandsumme." Account is taken especially of the fact that the thermionic phenomena are essentially surface phenomena. The expression for the free energy thus obtained is substituted in the general formulas for thermionic emission previously derived. The final formula thus obtained gives indications for the understanding of the fact that while for pure metals the "*A*" constant of Richardson's equation has almost exactly the universal value postulated by Dushman, it has a largely different value for oxides and adsorbed films. The question as to the existence of an electric double-layer on the surface of a metal is discussed, as well as the influence of such a layer on thermionic emission. It is shown that while the existence of such a layer follows from Schottky's "Equilibrium Theorems," the same theorems lead to the conclusion that the temperature change of the moment of such a layer is relatively small. Its value may be approximately estimated.

55. Measurement of electronic charge by shot effect in aperiodic circuits. N. H. Williams and H. B. Vincent, University of Michigan.—The theory of the probability variations of thermionic currents and their relation to the charge on the electron was investigated by Schottky. Hull and Williams measured the charge on electrons produced by thermionic emission, by photo-electric emission and by ionization of a gas. They worked with the high frequency currents set up in a tuned circuit by the Brownian fluctuations of the electron currents in a tube. The work here presented makes use of a five stage amplifier similar to the one they have described. The screen grid tubes were furnished by the General Electric Company. A pure resistance is substituted for the tuned circuit in which the shot effect is measured and an expression for the electronic charge in terms of the high frequency potential difference between the terminals of this resistance is developed. Both the mathematical derivation and the experimental procedure are considerably simplified. The results thus far obtained are in close agreement with the accepted value of the electronic charge. Measurements of shot effect have already thrown some light upon the nature of ionization and the mechanism of secondary emission and it is believed that this modification of the former method of measurement will increase the range of such investigations since the effects are larger and more easily measured.

56. Velocity distribution among thermionic electrons in vacuum and in hydrogen atmosphere. C. del Rosario, Yale University, (introduced by W. F. G. Swann).—The thermionic current from a tungsten filament to a coaxial cylindrical electrode was measured for different retarding potentials first in vacuum and then in hydrogen, keeping the temperature of the filament constant. The heating current was made intermittent to eliminate potential drop along the filament when the thermionic current was being measured, and it's effective value was kept constant to 1/20 percent by a Wheatstone bridge arrangement of which the filament was made one arm. The filament temperature, determined from data of Forsythe and Worthing ranged from 1800°K to 1990°K, and the pressure of hydrogen was varied from 0 to 0.22 mm Hg. The distribution of velocities among the electrons was found to follow Maxwell's law, contrary to the experience of other observers, for a gas in thermal equilibrium with the filament for both vacuum and hydrogen atmosphere.

57. **The adsorption of caesium on tungsten and oxidized tungsten.** JOSEPH A. BECKER, Bell Telephone Laboratories, Inc.—By means of a method previously described it is possible to determine the number of caesium atoms and ions that evaporate from a cm^2 of tungsten at various temperatures when the tungsten is covered to various extents. The results are exhibited by curves showing rates of evaporation versus fraction of the surface covered. A typical isothermal rises sharply at the origin, reaches a maximum for 1 percent of covering, then decreases exponentially until the covering is 20 percent when it again rises steeply. The first rise and fall are due to ions, the second rise to atoms. These curves show that as more caesium is adsorbed ions evaporate less readily while atoms evaporate more readily. They explain (1) why positive ion emission versus temperature curves show a steep rise at an upper critical temperature at which the filament cleans off spontaneously, and a steep decline at a lower critical temperature; (2) the lack of discontinuities in the electron emission at these same temperatures; (3) why the filament may be covered to two different extents separated by a dividing edge; (4) why this edge travels along the filament; (5) how changes in the caesium vapor pressure affect these characteristics.

58. **A new theory of ionic mobilities.** A. P. ALEXEIEVSKY, University of California, (introduced by Leonard B. Loeb).—Recently, Loeb has shown in HCl gas that the ions are probably clusters of molecules about a charged molecule. Previous theories have accounted for the mobility of ions assuming that the clusters consist of but a few molecules. In this paper it is shown that it is possible to account for the mobility of these ions by assuming that the ion consists of a droplet of liquid HCl, condensation being caused by the electrical forces of the charged molecule. Assuming that the force of attraction between ion and molecule is given by $f=(D-1)e^2/2\pi Nr^5$ where D is the dielectric constant, e is the electron, N the number of molecules per cm^3 and r the distance of the HCl molecule from the charge, one can calculate from the expression $vdp=((D-1)e^2/2\pi r^5N)dr$, using Van der Waal's equation, the radius R of the droplet which would be in equilibrium with any pressure of the gas. Placing the value of the radius so calculated in Epstein's equation for the mobility of a charged spherical droplet in an electrical field the mobility of the HCl ion is computed and found in good agreement with observed values. The equations also enables one to calculate the variation of the mobility with concentration in HCl air mixtures.

59. **Molecular structure and the relative mobilities of positive and negative gaseous ions.** LEONARD B. LOEB and A. M. CRAVATH, University of California.—Recently it has been shown by Loeb that the mobility of the negative ions in HCl gas is less than that of the positive ion. Condon made the suggestion that this was due to the presence of the H nucleus in the molecule which lay closer to the molecular surface than in most molecules. In a recent paper by Hund it is shown that both H_2O and H_2S exhibit the same general characteristics as HCl in the placing of the H nucleii. Mobility measurements have been made in these gases using the Franck modification of the Rutherford alternating current method. The mobilities of the positive ion in H_2S was 0.61 cm/sec per

volt/cm and that of the negative ion was 0.55 cm/sec per volt/cm. In water the mobilities were 0.62 and 0.56 cm/sec per volt/cm respectively. It is seen that these results are in agreement with the anticipation. The mobility values are relative to air, assuming 1.4 for positive and 1.8 for negative ions in cm/sec. per volt/cm.

60. Ether-drift experiments at Mount Wilson in February, 1926. DAYTON C. MILLER, Case School of Applied Science.—In February 1926, the ether-drift experiments were continued at Mount Wilson under very favorable conditions of weather. This series, consisting of 101 sets of observations involving 34000 readings, is the most extensive yet made for any one epoch. This epoch was chosen because, when combined with the epochs of 1925, it gives observations well distributed throughout the year. The new observations entirely confirm the results of the 1925 observations as announced at the Kansas City meeting. There is a periodic displacement of the interference fringes which is clearly systematic and cosmical in character; it is such as would be produced by a relative motion of the earth and the ether of 10 kilometers per second, the apparent apex of the earth's motion being a point in space having the right ascension of 255° and a north declination of 68°. The definitive values of the coördinates, from all available observations, are not yet determined. Causes for the observed phenomena other than relative motion are to be considered.

61. Faraday tubes and amperes rule. R. C. COLWELL, West Virginia University.—A new theory of Faraday tubes is outlined in which each tube is supposed to be made up of a succession of double doublets. These doublets have both electric and magnetic polarity. In a Faraday electric tube the electric poles are placed end to end and the magnetic poles are then perpendicular to the tube. In a Faraday magnetic tube, the electric poles are perpendicular to the tube. A Faraday tube always extends from a positive to a negative pole and shortens by an elision of the double doublets. When these doublets are elided they go out with a right hand twist thus giving rise to a closed electric or magnetic line of force. A lengthening of a Faraday tube reverses the direction of the closed magnetic (or electric) line of force. The single rule that "a shortening Faraday tube gives a right hand twist, a lengthening Faraday tube a left hand twist" is then sufficient to cover all cases of induced currents. It is also shown that this rule is equivalent to Ampere's rule regarding the attraction between two conductors which have currents in the same direction, so that Ampere's rule alone may be substituted for the many rules that are now given to determine the direction of an induced current.

62. The electric field of a charged wire and a slotted cylindrical conductor. CHESTER SNOW, Bureau of Standards.—The potential is found which is due to a fine wire (charged) in the presence of an outer shield at potential zero. This shield consists of a thin cylindrical shell, concentric with the wire, whose trace on a plane perpendicular to the latter consists of n equal, equally spaced circular arcs of a common circle. The problem is first simplified by a complex transformation $Z^n = z$, reducing it to that of a line charge in the presence of a single (incomplete) circular arc (a part of the circular arc $r = \alpha$). This problem is solved for any position of the line charge, the solution being effected first by a transformation $z = \alpha(i - z^1)/(i + z^1)$ which transforms the interior of this circle into the entire upper half of the z'-plane. The circular boundary then corresponds to the real axis of z'. This problem (that of a line charge in the presence of a finite straight line at zero potential) is again simplified by the transformation $z' = c \cos w$ which represents the entire z'-plane upon a semi-infinite strip in the w-plane. The proper (periodic) solution due to a line charge in this strip is then built up by an infinite series of images and their effect summed. By retracing the steps of the transformation, a solution in finite form is obtained for the original problem.

63. A new type of contact rectifier. L. O. GRONDAHL, Research Department, Union Switch and Signal Co.—A piece of copper with a layer of copper oxide formed on it at a high temperature is an unsymmetrical conductor of electricity. Ratios between high resistance and low resistance as high as 20,000 have been obtained. The unit consists of the oxidized piece of copper with a contact on the outer copper oxide surface made by means of a piece of lead or other soft metal applied under pressure. In a 1-1/2″ disc, the low resistance may be a small fraction of an ohm and it is therefore capable of carrying comparatively high current. The capacity of such a disc is represented by a d.c. output of 5 watts. Cuprous oxide is an electronic conductor and the rectifier is therefore permanent. The effects of voltage and of pressure on resistance are similar to the corresponding effects in contact rectifiers, the principal difference being in the magnitude of the resistances. The voltage characteristic results in a very slight distortion of the rectified wave. No forming is necessary so the rectifier is immediately operative when the alternating voltage is applied. The units may be assembled like cells in a battery to supply higher voltages or greater currents.

64. Electrolytic conduction of potassium through glass. V. ZWORYKIN, Westinghouse Elec. & Mfg. Co., East Pittsburgh.—Burt has reported the successful introduction of sodium into a thermionic vacuum tube by electrolysis, the filament of the tube being connected to the negative terminal of a d.c. supply while the positive terminal is connected to a crucible containing molten sodium nitrate into which the tube is immersed. Attempts to duplicate the experiment with potassium were unsuccessful, the failure being attributed to the smaller mobility of potassium ions. The author has repeated Burt's experiments with different glasses and finds that for a soda potash glass immersed in KNO_3 the metal introduced into the tube is primarily sodium while the glass itself is enriched in potassium at the expense of sodium and becomes unusually brittle. When a potash glass, free from sodium, is used, potassium of high purity passes into the tube without corroding or embrittling the glass. This seems to show that Burt's negative results with potassium were due primarily to the difference in dimensions and molecular forces of potassium and sodium ions.

65. The sodium voltameter. ROBERT C. BURT, California Institute of Technology. —This voltameter, mentioned in recent publications, using the electrolysis of Na through glass, has been modified in form by using metal contact with the glass instead of thermionic emission. The voltameter not only possesses a large advantage over the silver voltameter because of the simplicity of the operation involved and reproducability under ordinary working conditions where the limit of refinement is not demanded, but it has also been shown to yield results which are certainly correct to 1 part in 2000, and probably to 1 part in 6000.

66. Contact electromotive force of carbon. BRIAN O'BRIEN, Buffalo Tuberculosis Association, Perrysburg, N. Y.—The carbon surface was prepared by depositing a thin layer of soot from pure benzol on a platinum ribbon. The contact e.m.f. was measured against cupric oxide by the Kelvin method with a precision of 0.01 volt. Freshly smoked surfaces in air before outgassing were positive to CuO by about 0.40 volt, with some variation between different surfaces prepared alike. Reduction of pressure from atmospheric to less than 10^{-6} mm mercury without heating made carbon slightly less electropositive, reaching a steady state. Outgassing carbon at successive temperatures up to 1400°C (the CuO at all times cool) made the carbon less electropositive, finally becoming negative to the CuO by 0.11 volt. The outgassing-contact e.m.f. curves were fairly reproducible on a number of surfaces. An outgassed surface allowed to stand in air became more electropositive, but did not return to initial value. There was no evidence of a final value characteristic of a completely denuded carbon surface, as further heating at higher temperatures rendered the carbon progressively more electronegative.

Effect of mercury vapor. Allowing mercury vapor at a pressure of 0.001 mm in the tube did not affect the contact potential difference between the carbon and the CuO.

67. Dielectric constant of an electrolyte. EDWARD M. LITTLE, University of Illinois, (introduced by Jakob Kunz).—Dielectric constant is related to electric moment per unit volume just as permeability is to intensity of magnetization. The electric moment of an electrolytic solution decreases with ionization, and the dielectric constant for 100% ionization of the solute equals that for the pure solvent (corrected for volume change). A critical value of dielectric constant, k_c, is assumed, above which the molecular binding forces in the solution are weakened sufficiently to allow all molecules to ionize. For values of k below this, thermal agitation together with the dielectric constant, occasionally ionizes a solute molecule. In general, for initial values of k less than k_c and also for some values greater, there is less than 100% ionization of the solute. A relation between n (ionized molecules per cc) and the concentration, c (molecules of solute per cc) is found, and as a relation between k, n, and c is known (because of the relation between k and intensity of electrification) the relation between k and c is then obtained. It is approximately a hyperbola. The initial drop in the experimental curves is due to grouping of molecules around ions, thus decreasing the intensity of electrification and therefore the dielectric constant.

68. Piezoelectric quartz oscillators coated with metallic films. E. O. HULBURT, Naval Research Laboratory, Washington, D.C.—Recent experiments have demonstrated that a quartz piezoelectric crystal with the sides coated with films of platinum, copper, or other metals, may be used in a suitable electron tube radio circuit as an *oscillator*, i.e. a *generator* of sustained current oscillations. Electrical connection was made to the metallic films by soldering small wires to the films or by a brush contact. The natural frequency of the crystal was changed but slightly by the addition of the metallic film. This frequency change with the weight of the film, the effect of the films on the other frequencies and harmonics, the effects of temperature, gas pressure, etc., are being investigated in detail. W. G. Cady has shown that a piezoelectric crystal coated with chemically deposited silver will serve as a resonator in a radio frequency circuit; its use as an oscillator, however, appears to have been unsuspected. In fact previous experience would suggest that a metallic film adhering to the crystal may destroy its oscillating properties, just as an oil film is known to do.

69. A new phenomenon dealing with the action of electrostatic fields upon electric currents. PALMER H. CRAIG, University of Cincinnati.—If the Hall effect is caused by a magnetic deflection of the free electrons within a metal, an analogous effect should be produced by an electrostatic field. An electrostatic potential of 17,000 volts was applied to the edges of a bismuth film 7.5×3.0 cms in area and 0.045 cms thick, by means of copper rods separated from the bismuth by sulphur or plate glass insulation. When a current of one ampere flowed through the strip longitudinally, a net transverse potential difference of about 40 microvolts was measured between point contacts at the edges midway between the ends of the film. This was a net effect after correction had been made for thermal effects, leakage currents and other causes masking the true effect. The transverse potential decreased with decreasing electrostatic field, longitudinal current and thickness of the film, and was measured by a potentiometer arrangement sensitive to 0.01 microvolt. Moving the point contacts towards the end of the strip also decreased the effect. No effect was observed in copper, silver and aluminum and it was therefore concluded that if the phenomenon exists in these metals it is of very much smaller magnitude than that in bismuth. The magnitude of the Hall effect is approximately 611 times that of the new effect when comparing the magnetic effect at 1000 gauss with the electrostatic effect at 17,000 volts, the same bismuth film and a longitudinal current of one ampere being employed in both cases.

70. **Wave form of free electrical oscillations: self-capacity effect in multi-layer coils.** ALLEN ASTIN, New York University. (Introduced by J. C. Hubbard).—Observations have been made of the wave form of the free oscillations of a section, or sections of a multilayer coil by itself, and with added capacities, using the drop chronograph method developed by J. C. Hubbard (Phys. Rev., **9**, 529, (1917)). From the results periods, self capacities and damping factors of the coil are determined. Periods are determined to less than 1/10 per cent. The resistance is determined from the decrement. From a calibration of the contacts of the instrument, using a constant potential, the oscillation potentials are found to be in excellent agreement with those calculated from the constants of the circuits. With a coil of rectangular cross section of winding, with layer windings in several sections, but with the unused sections disconnected, the free periods are approximately independent of the number of sections used.

71. **The inductance of a helix made with wire of any section.** CHESTER SNOW, Bureau of Standards.—A formula has been derived for the inductance of a single layer helix which is to be used in absolute measurements of precision. It takes account of the helical nature of the winding and hence of the axial component of current in it. It is derived for any shape of wire section and is especially simple if this is symmetrical about each of two axes passing through its center of gravity. It is correct to the second order inclusive in small quantities like the ratio of the dimensions of the wire section to the radius of the cylindrical form. The current density is not assumed to be uniform but the formula applies (to the second order) to any current distribution which is developable by Maclaurin's theorem over the section of the wire. The formula is specialized and simplified for the cases of wires having circular or rectangular section. For windings of ordinary dimensions a precision is claimed of at least one part in a million.

72. **The resistance of condensers at radio frequency.** R. R. RAMSEY, Indiana University.—The condenser was placed in a "differential thermometer" made of two 800 cc pyrex glass beakers inverted on and sealed to two glass plates. Through each glass plate three holes were drilled. In two of these, electrical connections were placed and through the third a glass tube was sealed. To the glass tubes was fastened a U-tube filled with water. The height of the water in the tubes served to indicate the relative pressure in the two beakers. The radio condenser, which was an eleven plate variable condenser of "low loss" construction, was placed in one of the beakers and connected to the electrical connections which extended through the glass plate. In the second beaker a second condenser exactly like the first was placed, but this condenser was not connected to the terminals. A short piece of resistance wire was connected to the electrical terminals. The first condenser was connected into a radio frequency circuit and the resistance wire was connected to the electrical terminals. The first condenser was connected into a radio frequency circuit and the resistance wire was connected to a D.C. circuit. Then assuming that both beakers are exactly alike thermally when the pressures as indicated by the water in the U-tube are the same, we have I^2R in the high frequency side is equal to i^2r in the D.C. side. The average of a number of determinations at a frequency of 10^6 cycles, was .098 ohms. The individual results varied from .05 ohms to .15 ohms, the condenser being set so that the capacity was .00008 microfarads.

73. **Establishment of radio standards of frequency by the use of a harmonic amplifier.** C. B. JOLLIFFE and GRACE HAZEN, Bureau of Standards.—One method used by the Bureau of Standards in establishing radio standards of frequency consists in the "stepping up" from a known standard audio frequency to a radio frequency by the use of harmonics. The low-frequency output is carried through an amplifier arranged to distort and so produce harmonics. By means of tuned circuits a harmonic is selected which in turn serves as a fundamental for further distortion and amplification to give the desired frequency with sufficient power to operate the frequency meter under standardization.

A fixed radio-frequency generator such as a piezo oscillator, or a fixed audio-frequency generator such as an electric-driven tuning fork, can likewise be standardized by the use of the harmonic amplifier with the addition of a sonometer for measuring an audio-frequency beat note produced by a harmonic from the standard audio-frequency source and the fundamental or harmonic from the fixed-frequency generator. The frequency of the beat note is impressed on the steel wire of the sonometer by means of a telephone receiver magnet. The vibration frequency of the wire is calculated by means of the constants of the wire and the tension applied.

74. Cooperative investigation of radio fading. J. H. Dellinger, C. B. Jolliffe and T. Parkinson, Bureau of Standards.—Signal intensity fluctuation is one of the chief barriers to reliable long distance reception of broadcasting and of the higher radio frequencies. With a view to securing quantitative data on this phenomenon the Bureau of Standards invited a number of university and other laboratories to engage in a co-operative program of fading measurements. This report summarizes the progress made in 1925 when five series of simultaneous observations were made on certain specially arranged transmissions from broadcasting stations. Twenty laboratories in the eastern half of the United States were engaged in the work. The measurements consisted of recording graphically variations of deflection of a galvanometer connected to radio receiving apparatus so as to indicate directly variations in the received field intensity. These records were supplemented in some cases by absolute measurement of the field intensity and by simultaneous continuous records of direction variation. The measurements yielded data of value on the characteristic radio wave phenomena during a solar eclipse, during the sunset period and the variations throughout the whole diurnal cycle.

75. Reception currents from a loop antenna. R. C. Colwell, West Virginia University.—If the oscillations in the four sides of a loop antenna are regarded as made up of the oscillations of a succession of vibrating doublets, an integration around the the loop will give the resultant electric vector for any point in space. For the two vertical sides of the loop, the electric intensity takes the form $E_\theta = (2I \tan \theta / cr_0)(1 - \cos 2\pi h \cos \theta/\lambda r_0)^{\frac{1}{2}}(1 - \cos 2\pi a X/\lambda r_0)^{\frac{1}{2}}$ This equation shows that a loop has a directional effect high up in the air as well as along the ground. If the integration is taken over one vertical and one horizontal side, we have the electric intensity due to a bent antenna. The resulting equation is in the form

$$E_\theta' = (Ic/r_0)\ ((A + B \cos \alpha)^2 + (C + D \cos \alpha)^2)^{\frac{1}{2}}$$

The cos α changes sign when the azimuth is 90° in such a way as to give a directive effect to the wave sent out from this antenna; the intensity being greatest for azimuth 180° and least for azimuth 0°.

76. A ballistic galvanometer as an integrating instrument. H. L. Curtis and C. Moon, Bureau of Standards.—The formula for the capacitance when using Maxwell's absolute bridge is derived assuming that the time integral of the current through the galvanometer is zero. This paper shows the conditions which must be fulfilled by a galvanometer in order that it will correctly integrate the current. With all integrating galvanometers the torque produced by the current through the coil shall at every instant be proportional to this current. This will be the case only if the coil is non-magnetic and if the current through the coil does not affect the field of the permanent magnet. This last condition can be experimentally realized by finding the position of the coil where the reversal of the applied electromotive force does not change the galvanometer reading. A second requirement applies only to conditions similar to those in a Maxwell bridge. These conditions are such that the curve of motion of the galvanometer coil as a function of time is a series of parabolas. In order that the time integral of current shall be zero, the time integral of deflection must also be zero. This requires that the excursions shall be on both sides of the galvanometer zero, but not an equal amount on the two sides. The ratio on the two sides is as two to one.

77. Magnetostriction in permalloy. L. W. McKeehan and P. P. Cioffi, Bell Telephone Laboratories, Inc.—The specimens examined were well-annealed 1 mm wires, 40 cm long, of iron, nickel, and permalloys containing from 46 to 89 percent nickel. Changes in the magnetization were measured ballistically. Changes in the length of part of the specimen were multiplied two million times by a mechanical lever, an optical lever, a multiple slit, a photo-electric cell and a sensitive galvanometer. Measurements were made with or without tension. The rate of increase in magnetostriction with magnetization, at zero magnetization, was zero in all cases. Permalloys with less than 81 percent nickel expanded, those with more than 81 percent nickel contracted when magnetized. Tension reduced the expansions and increased the contractions. The theory of atomic magnetostriction (Phys. Rev. **26**, 274, (1925)), explains the new results and suggests that orientation of the magnetic axes of iron and nickel atoms, precisely like that due to the application of magnetic fields, may be effected by mechanical stresses within the elastic limit. Changes in electrical resistance (Phys. Rev. **23**, 114, (1924)) support this view.

78. Hall effect in mono-crystalline copper. P. I. Wold, Union College.—The Hall effect has been measured in a single crystal of copper in the form of a rod 15 cm long and .55 cm in diameter. The crystal was cubic with an axis nearly coincident with the longitudinal axis of the rod. Transverse contacts were obtained by copper terminals spring pressed against the sides of the rod, the rod being placed in a holder which permitted rotation about the longitudinal axis. The Hall constant varied with rotation, but only by relatively small quantities which were irregular and apparently due to difficulty in maintaining stable transverse contact. If the Hall constant parallel to an edge of the crystal cube is R_1 and that at right angles thereto is R_2, the results are in agreement with the relation that in intermediate directions the resultant constant is $R=R_1 \cos^2 x+R_2 \sin^2 x$. In the case of a cubic crystal $R_1=R_2$.

79. The effect of small amounts of silicon on the thermo-magnetic change point "*A2*" in mild steel. F. C. Farnham, New York University (Introduced by H. H. Sheldon).—Tests have been made on samples of steel containing .25 percent carbon with varying silicon content up to 3 percent. It is observed that for small amounts of silicon, up to about .5 percent, the point "A2" is lowered rather rapidly; for added amounts, up to about 2 percent, the lowering of "A2" is much less; and for amounts between 2 percent and 3 percent the rate of lowering of "A2" is again greater. From these results it is evident that the presence of the carbon greatly modifies the effect of silicon as observed in ferro-silicon alloys.

80. Magnetic moments of the alkali metal atoms. John B. Taylor, University of Illinois, (introduced by W. H. Rodebush).—The results previously reported on sodium (Kansas City meeting) have been confirmed, showing that the neutral sodium atom possesses a moment closely equal to one Bohr magneton. Potassium has also been investigated and shows, likewise, the single magneton value.

The amounts of deflection or splitting of the atomic rays of sodium and potassium are related inversely as the temperatures of evaporation, in accord with the equations for the effect. Distinct images of the divided rays have been obtained.

81. The Zeeman effect, the Stern-Gerlach experiment and the magneton. Jakob Kunz, University of Illinois.—Landé and Sommerfeld have given a classification of the anomalous Zeeman effect, which makes it possible to determine the number of magnetons in an atom if the multiplicity, the ground term of the atom and the inner quantum number are given. These numbers have been supplied to the writer by P. D. Foote for most of the elements. The number of "lines" to be expected in the Stern-Gerlach experiment, and the number of Bohr magnetons has been calculated. It has been shown moreover that especially for the rare earth elements the agreement between these calculations and recent measurements is satisfactory.

82. Direct absolute measurement of acoustic impedance. G. W. STEWART, University of Iowa.—Advantage is taken of the author's theory of the transmission in an acoustic line with an attached branch which alters the intensity and the pressure phase of the transmitted sound. By the measurement of the relative intensities and phases with and without the branch present, it is possible to obtain the components Z_1 and Z_2 of the impedance, $Z=Z_1+iZ_2$, of the branch. If S is the area of the conduit, P_0 and P_0' the two pressure amplitudes, ϵ the change in phase, ρ the density of the medium, a the velocity of sound therein, $Z_1=(\rho a/2S)\ [A/(A^2+B^2)]$ and $Z_2=(\rho a/2S)$ $[B/(A^2+B^2)]$, wherein $A=(P_0/P_0')\cos\epsilon-1$ and $B=-(P_0/P_0)\sin\epsilon$. The method involves only the *relative* magnitudes of pressure amplitudes and the direct measurement of phase change, the knowledge of density and velocity being sufficiently accurate. In the present application the pressure ratio is determined by altering a comparison source, and the phase is measured directly. The method involves only one simple absolute measurement and is a strictly acoustic method somewhat analogous to methods of measurement long used in electricity.

83. Effect of amplitude on the frequency of a tuning fork. C. MOON and H. L. CURTIS, Bureau of Standards.—There has been devised a method for the precise rating of a tuning fork by comparison with a pendulum. A series of flashes of twice the fork frequency are obtained by means of slits in a pair of vanes carried by the prongs of the fork giving images on a moving film, formed by two concave mirrors, one attached to the pendulum and the other to the pendulum support. The frequency of the fork is computed from the trace on the film. An accuracy of five parts in a hundred thousand can be obtained from the record over a single second of time. Two 100 cycle forks, one of steel, the other of elinvar were studied. When vibrating freely showed nearly a linear increase in frequency with decreasing amplitude. The elinvar fork increased ten parts the steel fork three parts in a hundred thousand as the amplitude decreased from 1.0 mm to 0.25 mm. With either of the forks maintained at a constant amplitude by a vacuum tube drive, the frequency could be changed by a part in ten thousand by varying the condiions in the tube circuits. Hence there can be no proper discussion of the effect of amplitude on the frequency of a driven fork.

84. Hysteresis due to the Ewing effect in the flexure of bars. G. H. KEULEGAN, Bureau of Standards, (introduced by L. J. Briggs).—Boltzmann's theory of elastic time effects does not always account for the entire hysteresis observed in the deformation of an elastic body during a closed load cycle. The author, therefore, has made an attempt to formulate an additional theory of hysteresis which is independent of time effects and calls such hysteresis the "Ewing effect." The basis of the theory is the assumption that the stress-strain curve of an elastic body, instead of being a straight line, consists of a symmetrical loop. The deductions from the theory as applied to the flexure of bars are as follows: (a) In the flexure of bars the energy lost owing to the "Ewing effect" varies with the third power of the maximum load of the load cycle and with the fourth power of the length of the bar. (b) The distribution of hysteresis is parabolic and is independent of the maximum load and of the length of the bar. Again, a general deduction from the theory is that the loss of energy per unit volume for a tensional stress range σm is $1/3\beta\sigma_m{}^3$. Experiments gave $\beta=1.33\times10^{-6}$ ergs cm^3 per kg^3 for Armco iron; so that energy loss per cubic centimeter due to hysteresis is 26,000 ergs for a stress range of 3900 kgs per cm^2.

85. The expansion of copper from absolute zero to the melting-point. Thomas A. Wilson and Wheeler P. Davey, General Electric Company.—Copper bars of rectangular cross-section, 3/8 inch on a side and approximately 30 cm long, were supported on powdered alumina in an alundum tube wound with a molybdenum heating coil lagged with a wrapping of asbestos 2½ inches thick. The tube extended 2 inches beyond each end of the copper so minimizing end cooling. Two holes 3/8 inch square drilled through the tube and asbestos permitted reading the position of the ends of the copper with a horizontal cathetometer. The experiments were conducted in a hydrogen atmosphere. The power through the heating coil was increased approximately 100 watts every 24 hours, at the end of which period a reading was made. At temperatures near the melting-point, readings were made quite frequently. Two experiments gave the linear expansion of copper per cm length from room temperature (27°C) to the melting-point as .0257 cm and .0264 cm . With data from Landolt-Bornstein, the calculated expansion from absolute zero to 27°C is .0034 cm per cm length, making the total expansion from absolute zero to the melting-point .029^{1} cm per cm length.

86. The expansion of crystals from absolute zero to the melting point. Wheeler P. Davey, General Electric Company.—In a face-centered cubic crystal each atom lies in a "pocket" formed by three adjacent atoms of a 1 1 1 plane (the slip plane) so that the four atoms form a tetrahedron. At 0°K the "atomic domains" are assumed to be in contact. It seems plausible that, in such a crystal 12½ percent of the tetrahedra must expand 4½ percent along each edge before all the surface atoms can leave the solid. But at any instant 12½ percent of the tetrahedra are 1.7 times the most probable size. A linear expansion of 2.6 percent from 0°K is therefore a prerequisite to melting for a face-centered cubic crystal. Added to this will be the expansion occurring while the atoms take up additional energy to overcome cohesion. Expansions calculated from the literature are Al 2.4 percent; Mg (having an analogous structure), 2.4 percent; Ag 2.3 percent; Cu 2.4 percent; Ni 2.9 percent. These are probably all low because of extrapolations. Recent measurements of Cu (see previous abstract) indicate 2.9 percent. Body-centered cubic crystals require no expansion except what occurs while overcoming cohesion. Na and K become non-crystalline before melting. W expands 2 percent corresponding to its high interatomic attraction.

87. Thermal properties of butane, isobutane, propane, and ethane. Leo I. Dana, Linde Air Products Company, Buffalo, N. Y.—The investigation is intended to cover the thermal properties of these liquids in the saturation region over the range of pressures and temperatures required for the use of these gases as refrigerants. The latent heats of vaporization and the specific heats of the liquids of ethane and propane have been determined from −40°C to +30°C; of isobutane and butane from −13°C to +30°C. An aneroid calorimeter, enclosed by a vacuum jacket, operating adiabatically and thus avoiding heat leak corrections, was employed. The vapor pressures of the first three have been measured from one half atmosphere absolute to about 6 atm. abs. and the measurements are being extended to higher pressures. The liquid and vapor densities of the first three gases have been measured from 0°C to 60°C. New forms of cryostats have been constructed for the low temperature measurements.

88. Thermal conductivity of lithium, sodium and lead to −250°C. Charles C. Bidwell, Cornell University.—The bar method of Forbes was modified as follows. The metal rod, centered in a large test tube, was placed in a constant temperature bath and heated by a coil at the upper end. Air convection in the tube was stopped by cardboard disks through which the rod was threaded and which were spaced at short intervals along the rod. Temperature gradient was determined by thermojunctions spaced along the rod. Cooling curves were obtained on smaller lengths of the rod similarly mounted. With mean temperature not exceeding 15° above bath temperature accurate values of

k were obtained. Values for lead from $-250°$C to $+100°$C taken to test the method agreed well with the best recorded values. Lithium shows a linear increase in k from 0.15 at 0°C to 0.20 at $-200°$C, thereafter rising sharply to 1.00 at $-246°$C. Above 0°C a minimum occurs at $+40°$C and an increase thereafter to 0.17 at $+140°$C. Sodium shows a linear increase from 0.28 at $-40°$C to 0.40 at $-240°$C. Above $-40°$C an increase occurs to 0.35 at 0°C and thereafter a decrease to 0.28 at $+65°$C. The breaks in these lines correspond to breaks previously reported in electrical conductivity and thermo-electric power lines for these metals.

89. Thermal conductivity of metals at high temperatures. M. F. Angell, University of Idaho.—This paper describes a continuation of former work with improved methods. The metal is heated electrically in the form of a long hollow cylinder. In the earlier experiments the heat flow was assumed to be radial at a point midway between ends, but in these experiments this assumption is made for the point of maximum temperature along the cylinder. The thermal conductivity is calculated from the temperature gradient along the radius at this point and from the energy transmitted. Complete curves of the thermal conductivity from 50°C to the melting point are given for copper, zinc and lead. For copper the thermal conductivity was found to be .92 at 50°C, decreasing very slowly to .90 at 500°C, then more rapidly to .8 at 1000°C. The conductivity of zinc decreases from .265 at 50°C to .215 at 400°C. The conductivity of lead decreases from .082 at 50°C.

90. The ratio of heat losses by conduction and by evaporation from any water surface. I. S. Bowen, California Institute of Technology.—From theoretical considerations it is shown that the process of evaporation and diffusion of water vapor from any water surface into the body of air above it is exactly similar to that of the conduction or "diffusion" of specific heat energy from the water surface into the same body of air. Due to this similarity it is possible to represent the ratio R of the heat loss by conduction to that by evaporation by the formula, $R=.46(T_w-T_a)P/(P_w-P_a)760$, where T_a and P_a are the original temperature and vapor pressure of the air passing over the lake, and T_w and P_w are the corresponding quantities for the layer of air in contact with the water surface. The substitution of R times the evaporation loss for the value of the conduction heat loss in the Cummings equation for evaporation makes it an exact equation for the determination of evaporation from any water surface in terms of the net radiant energy absorbed by the water and the heat stored in the water.

91. Surface tension of sodium. F. E. Poindexter, Washington University.—The surface tension of sodium was determined in a high vacuum at a series of temperatures ranging from 105°C to 245°C. A modified flat drop method was used. The values taken from the best mean straight line through the experimental points gave the values of 222 dynes per cm at 100°C and 211 at 250°C. This gives a temperature gradient of .072 dynes per degree. From the Eotvos relation $\gamma v^{2/3}=k(T_0-T)$ we get upon differentiating with respect to T, $v^{2/3}d\gamma/dT=-k$, where γ is the surface tension, v is the volume of a gram atom, T is the temperature and T_0 and k are constants. Taking the density of sodium as .91 at 100°C, we find $v=8.6$. This together with the experimental value of .072 for $d\gamma/dT$ gives us $k=.62$. This is taken to mean that the molecules in liquid sodium are polyatomic, since the value of k for non-associated liquids is 2.2.

92. Pressure distribution over airfoils at high speeds. L. J. Briggs and H. L. Dryden, Bureau of Standards.—The forces exerted on a body by an airstream of speed not greater than a few hundred feet per second depend on the airspeed, V, size of the body as given by a linear dimension, L, air density, ρ, and viscosity, μ, in the manner described by the equation

$$\text{Force}/(\tfrac{1}{2}\rho V^2L^2)=\phi(VL\rho/\mu).$$

At high speeds the influence of the compressibility of the air becomes appreciable and the force coefficient is a function of the ratio of the air speed to the speed of sound as well as of the Reynolds number, $VL\rho/\mu$. The variation of force coefficient with Reynolds number is small whereas the variation with speed ratio has been found by the authors, together with G. F. Hull, to be large. The work now described gives a more extensive and systematic series of observations on airfoil sections of 1 inch chord including observations of flow near the surface. The large changes in forces were found associated with a breaking away of the flow from the surface. The pressure distribution furnishes data to the propeller designer regarding the load distribution encountered at high speeds. The paper will be published as a Technical Report of the National Advisory Committee for Aeronautics.

93. **Compensation of altimeters and altigraphs for air temperature.** W. G. BROMBACHER, Bureau of Standards.—The altitudes of aircraft are usually determined by an altimeter, which is an aneroid barometer calibrated to an altitude-pressure relation containing an arbitrary altitude-temperature assumption. For the accuracy required in aeronautics, altitudes should be determined by both pressure and temperature measurements. It is difficult to take account of the mean temperature term of the barometric formula mechanically in an instrument. The following new relation based on the summer, winter, and yearly averages of observations of upper air temperatures at latitude 40° in the United States is presented as a substitute. Up to 30,000 feet: $dP/dt = A_h$, (1) where P is the pressure and T the absolute temperature at the altitude h, and A_h is a constant for any one altitude. Further, values of A_h give values of K varying from 0.0023 to 0.0038 in the following important relation for instrument work, $A_h/(P_0 - P) = K$, (2) where P_0 equals 760 millimeters of mercury pressure. Altitudes according to relations (1) and (2) can be indicated by using a temperature element ("air temperature compensation") or a manually operated device to modify the multiplication of the mechanism ("ground temperature compensation"). The manually operated device modifies the multiplication according to an average value of K and the temperature dial is graduated in terms of ground level temperatures.

94. **The effect of a high temperature in disrupting ice.** HOWARD T. BARNES, McGill University.—Our knowledge of the mode of transfer of heat across very steep temperature gradients is practically nil. The author has been experimenting in this field by driving a powerful energy charge into solid ice cooled below the freezing point. An intense exothermic reaction is rapidly generated by burning a mass of aluminum and the temperature is raised in 5 to 8 seconds to 2500°C. The disruption of the ice below 0°C is observed. Ice is, in this way, converted into a high explosive, the atoms being driven out of the molecules without melting the ice. In large masses a slow explosion occurs which resembles the reaction of black powder set off at a low temperature rather than the sudden detonation of dynamite. Ordinary welding thermit has been used conveniently, since that material is not in itself explosive. Application of this method has been made practically, as it offers a powerful means for relieving ice accumulations.

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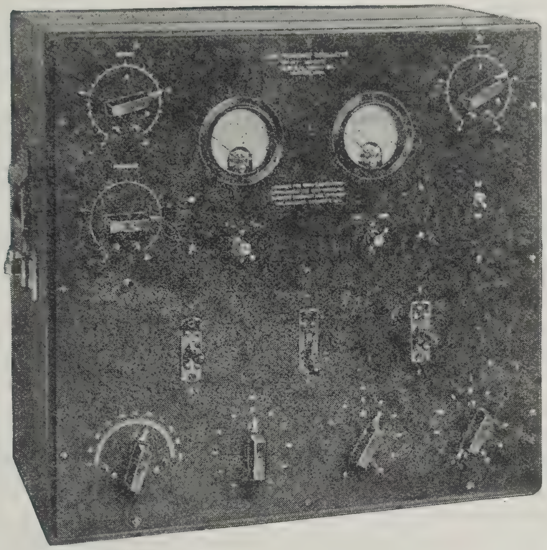

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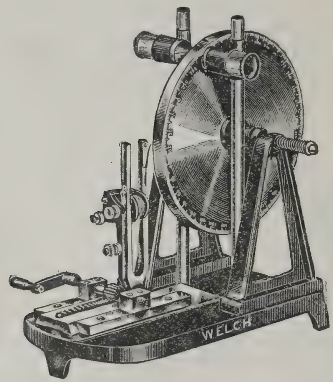

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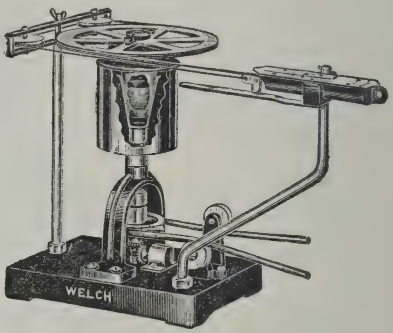

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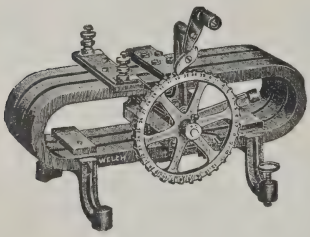

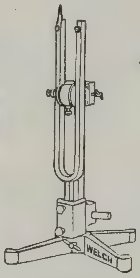

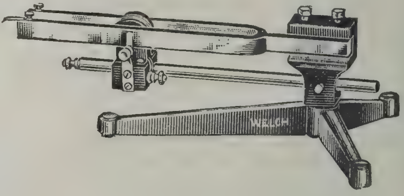

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As a summary the abstract should give briefly the conclusions of the article, important advances in experimental technique and theory, and all numerical results of general interest that may be conveniently given including all that might belong in a hand book and table of constants. It should give all the information that readers who are not specialists in the particular field involved might desire to know about the article thus saving them the time and trouble in referring to the article itself. Experience has shown that in general the length of the abstract should be from four to eight percent of the length of the article.

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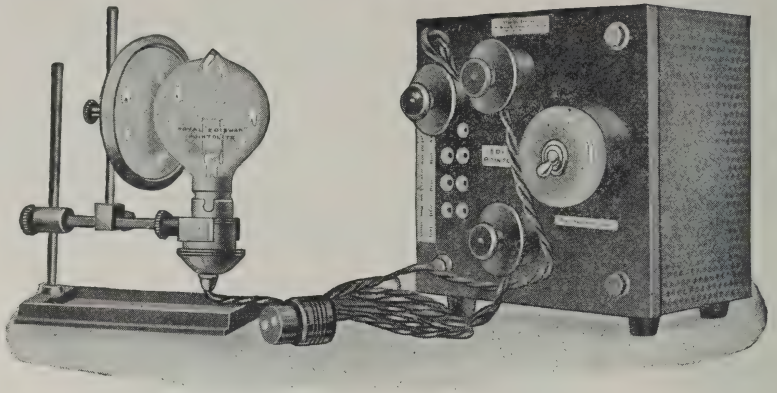

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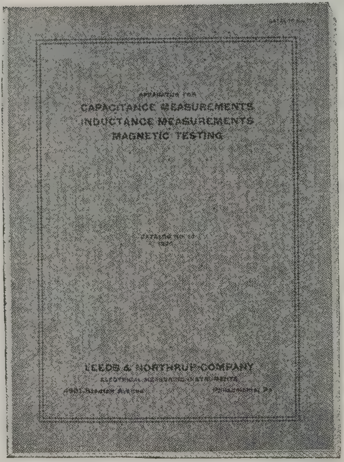

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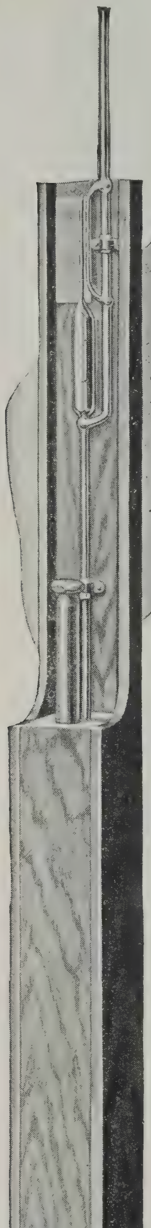

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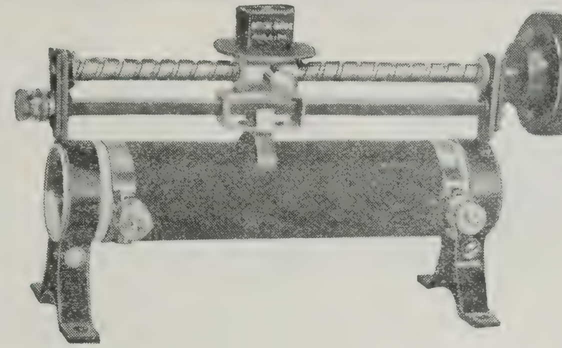

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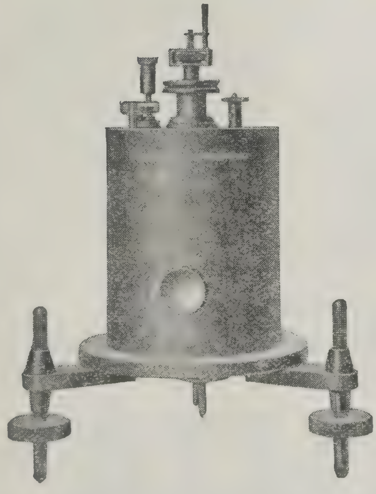

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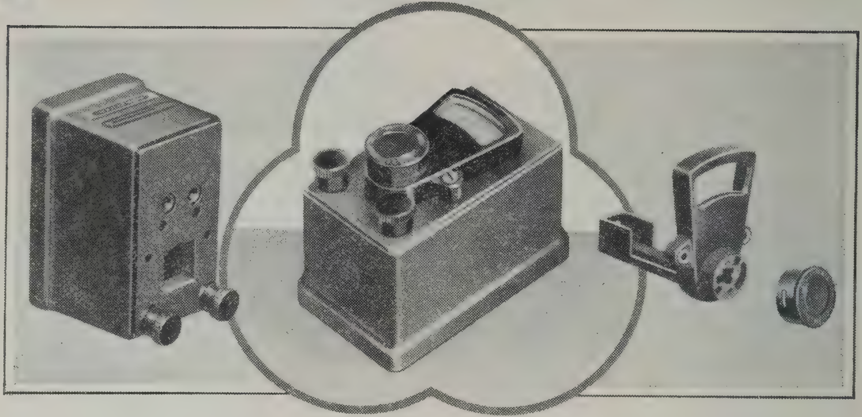

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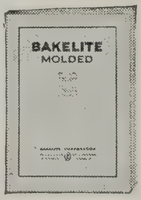

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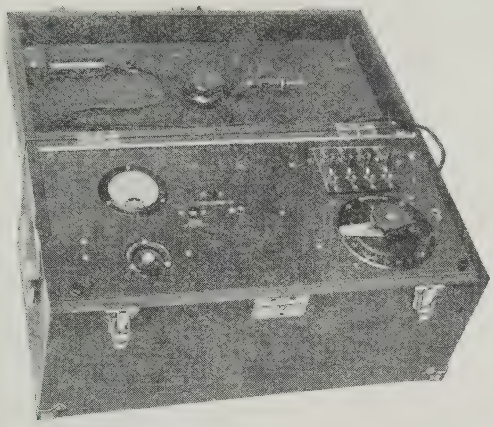

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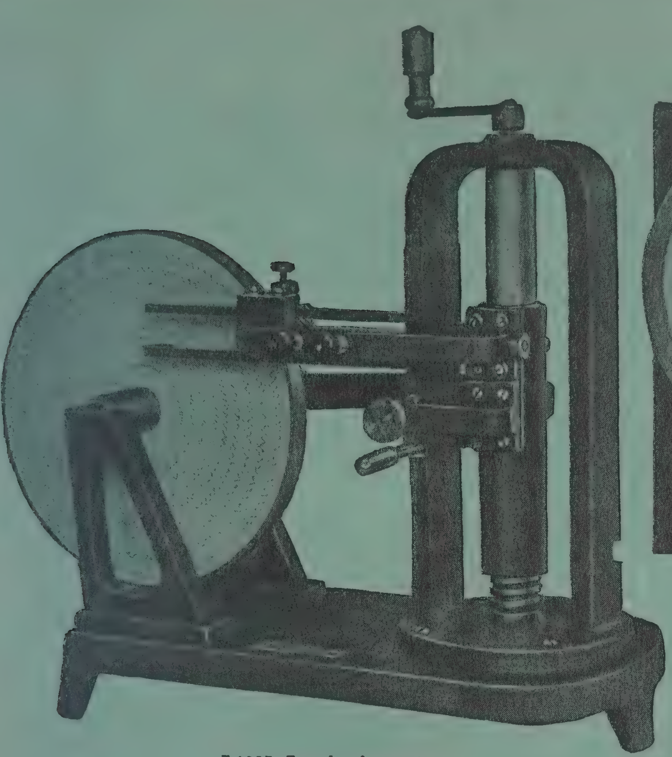

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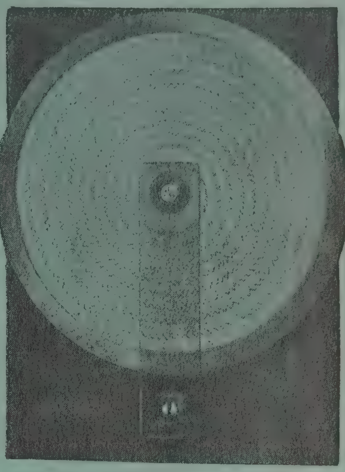

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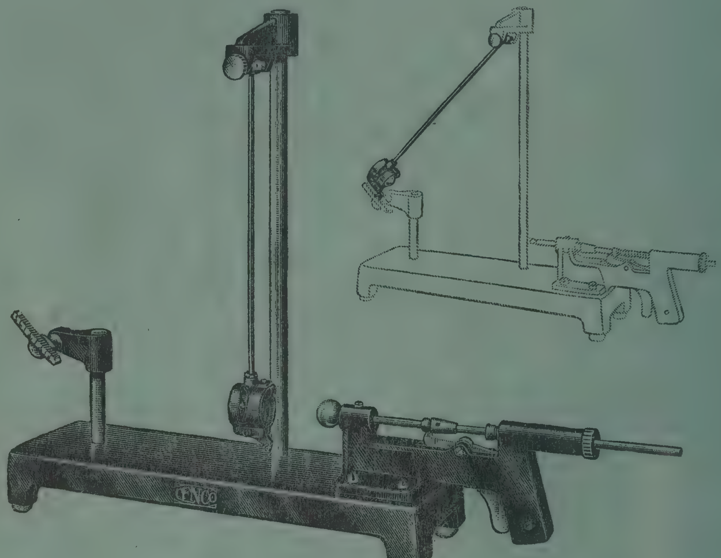

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